Sources and management of water colour in the river Tees

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Sources and Management of Water Colour in the River Tees

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One volume

Submitted to the University of Durham in partial fulfilment of the requirements for the degree of Doctor of Philosophy

2006

Abstract

Over recent decades, a wide range of rivers and lakes draining peat-dominated catchments across the UK have exhibited statistically-significant increases in water colour and dissolved organic carbon (DOC) concentration. This has implications for the carbon budget of those peatlands, and for the long-term viability of water treatment works which must remove the colour in the treatment process. Suggested causes for such increases include lower water tables in the peat, and changes in the peat chemistry through decreasing atmospheric acid deposition.

One factor potentially affecting the peat water tables, and therefore possibly related to the increases in DOC, is the practice of peatland drainage, which may affect both the production of DOC and the hydrological behaviour of the peat. Drainage is no longer believed to be beneficial in increasing the amenity value of peat and so there is a need to understand whether blocking the drains will be an effective strategy in decreasing DOC export and mitigating the observed increases at water treatment works.

This thesis presents the results of monitoring individual blocked drain, unblocked drain, and stream catchments. The results are used to construct detailed DOC export budgets and to compare the behaviour of the catchments. This enables identification of the extent to which drainage increases DOC export; of differences in behaviour between blocked and unblocked drains, and of whether drain blocking is likely to reverse any such increase in DOC export.

Results from these individual small catchments are considered in the context of the overall DOC export across the larger scale catchment of a large water treatment works. DOC sources across the larger catchment were also monitored and, using novel statistical techniques, catchment export is related to catchment properties including the presence of drainage. These results are used to assess the likely benefits of a large scale drain blocking programme with respect to the DOC concentration observed at the water treatment works.

Results are presented showing that drainage does substantially increase the DOC export from peat, with DOC export being highest from flat, extensively drained peat areas. Blocking does decrease the export from individual drain catchments, but not to pre-drainage levels, even a decade after blocking. The decreases due to blocking are shown to be due primarily to changes in the hydrological behaviour of the drains rather than changes in the production of DOC.

Therefore a catchment-wide drain blocking programme is recommended as a strategy for reduction, but not total amelioration, of the increasing DOC trend that is observed at water treatment works. However, before this is implemented further understanding of the large scale changes in peatland hydrology that may follow blocking will be required, as the results do not indicate a reduction in DOC production.

Declaration and Copyright

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. Where relevant, all material which is the work of others has been acknowledged.

Signed:
Harry Gibson

Date
30th November 2006

Acknowledgements

I would firstly like to thank Dr Fred Worrall for his supervision, approachability, drive and advice throughout the project. Professor Tim Burt provided an excellent sounding board for ideas and an invaluable source of advice.

Dr Chris Ottley provided expert technical guidance in experimental work and Dr Chris Johnson provided advice ranging from laboratory techniques through to thesis planning; I am grateful to both. Alan Edwards and Lindsay Waddell, estate mangers at the Allenheads and Raby Estates respectively, were extremely accommodating of our wishes to dig holes in and clutter up their grouse moors. Their flexibility in allowing access is appreciated, as was the occasional tow to remove the department vehicle from snow-filled ditches. James Rowson provided invaluable help on fieldwork and demonstrated that my water sample collection was by no means the most time-consuming thing or tedious thing to do on a peat bog in the middle of winter. Thanks also go to Alex Staden, previously at English Nature, for providing access to, and advice on digitising, the aerial photography datasets. Without funding from Northumbrian Water for the first eighteen months, the project would not have existed; I hope their money was well spent.

Thanks go to the others in Durham who enlivened my second four years here. Alona Armstrong and Rob Dunford showed me the way to the Other Side of the Geology / Geography building, where I picked up a vast amount of useful data analysis techniques. Geoff Nowell let me fly a wider range of kites than I could ever afford. Richard Turner provided endless fascinating diversion and conversation.

I am extremely grateful to both my parents. They probably saw this in me years ago but without their patience and financial support it would not have been possible.

Above all, thanks go to Naomi for her infinite patience and support. This work would not have happened without her.

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1 Introduction

1.1 Project Rationale

1.1.1 The problem at Water Treatment Works

Broken Scar is a water treatment works in Darlington, England, owned and run by Northumbrian Water Ltd. The works obtains its water from the River Tees and is responsible for providing fresh water to approximately 100,000 people across Darlington and the surrounding area, making it the eighth largest water treatment works in England.

Long term records exist for the observed riverine dissolved organic carbon (DOC) levels, as water colour, at Broken Scar (Worrall et al, 2003a). These data, illustrated in Figure 1.1 and backed up by empirical observations from managers of the water treatment works, suggest an approximate doubling in average water colour levels over the last 30 years. Since colour is generally proportional to the concentration of DOC (e.g. McKnight et al, 1985), this implies a similar increase in the concentration of DOC in the river water at the treatment works.

This trend is not confined to the Broken Scar catchment: records for DOC concentration at a wider range of sites across the UK show similar increases in the majority of cases. Worrall et al (2004a) examined records from 198 sites around the UK and found significant ($P<0.05$) increases in DOC concentration at 153 sites. The remaining sites showed no significant trend: no sites showed a significant ($P<0.05$) decrease. Freeman et al (2001a) found significant increases over a period of 12 years at 20 of 22 sites.

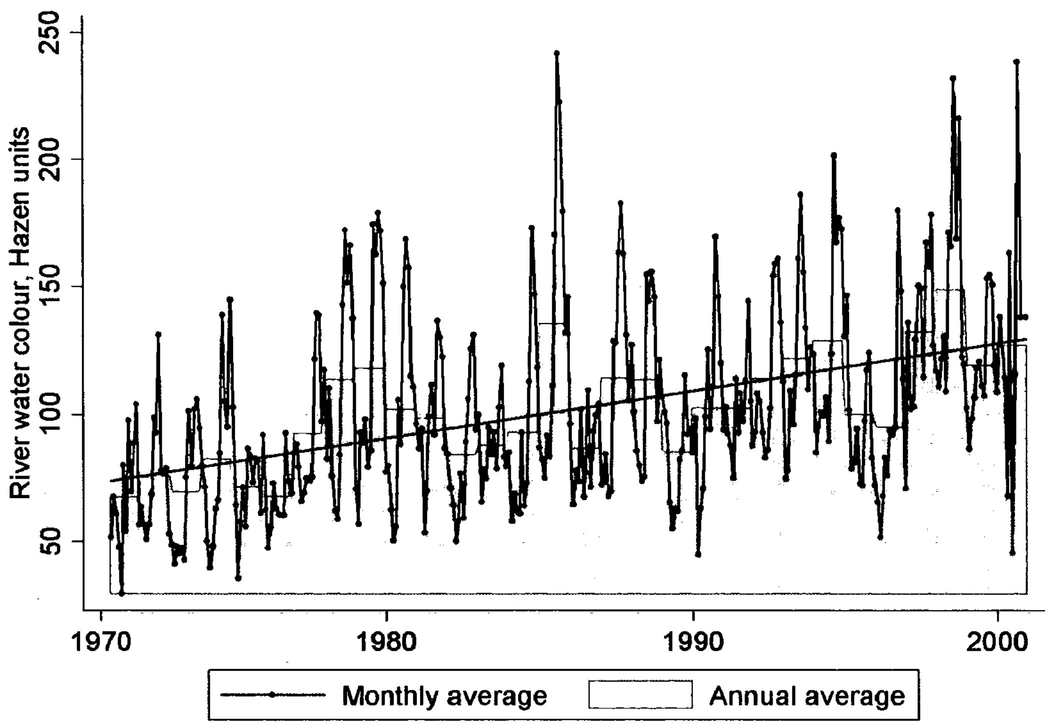


Figure 1.1 River water colour in Hazen units as observed at Broken Scar water treatment works.
Adapted from Worrall et al (2003a). Least-squares trend fit is significant with $P<0.0005$. On these data DOC (mg l^{-1}) = 0.051(Hazen) + 1.09 (R^2 = 0.82, Worrall et al, 2003a).

There are strict requirements governing the colour levels of output (treated) water from water treatment works. The prime motivation for such limits is the unwanted formation of disinfection by-products (DBPs) such as trihalomethanes (mainly chloroform, $CHCl_3$, but also brominated THMs where bromide is present) and haloacetic acids (mono-, di-, and trichloroacetic acids). Such compounds are formed upon chlorination of water which contains organic compounds such as those that make up DOC (Singer, 1999). Trihalomethanes are of particular concern because their ingestion has been linked to bladder and rectal cancer (Morris et al. 1992, Hildesheim 1998). Additionally, due to the fact that the chlorine is consumed by formation of these compounds, the residual chlorine required to provide ongoing disinfection while the water is transported to the consumer is not present. Furthermore not only does DOC present in the water enable microbial regrowth by removing residual free chlorine, but it actually encourages the process, as it acts as a food source for microbial growth (Fearing et al 2004). DOC levels are also of great concern beyond the context of drinking water treatment, as transport of DOC to the marine environment via rivers is a significant part of the global carbon cycle. DOC dominates the total carbon flux in many peatland streams (Dawson et al, 2002) and Hope et al (1994) estimate the global riverine flux to be between 1 and 10^{11}kg C yr^{-1}; despite the inevitable large uncertainty in such estimates any increase in DOC is of concern.

1.1.2 Options for DOC removal

DOC remaining in the water at the filtration stage of treatment causes further problems through clogging of microfilters and blocking adsorption sites in granular activated carbon (GAC) filters (Fearing et al 2004), a process known as "blinding". DOC compounds should therefore be removed in the water treatment process before microfiltration, GAC filtration, or chemical disinfection. The conventional treatment method for removal of the organic compounds causing water colour is coagulation and flocculation followed by removal of the floc through a combination of sedimentation in settling tanks and filtration. Coagulation is achieved most commonly through the addition of iron sulphate compounds or alum, which causes negatively charged "dirt" particles and compounds to clump together, attracted to the positively charged coagulant (Adgar et al, 2005). Where filtration is through granular activated carbon this can also contribute directly to colour removal, through adsorption of colloidal or dissolved DOC in addition to the trapping of floc particles, but this shortens the lifespan of the GAC, reducing its effectiveness at adsorbing other pollutants, and increases costs.

The amount of colour that can be removed by coagulation and flocculation is limited by the capacity of the mixing and settling tanks and, due to the holding time required for the process, by the current demand for fresh water. Furthermore, the flocculation chemicals become a major cost in the water treatment process. Newer approaches to DOC removal are also being developed such as the use of the proprietary magnetic ion exchange (MIEX®) resins. The MIEX resin is an anion exchange resin, used in the form of small beads, which is artificially manufactured to encompass many of the characteristics leading to high DOC adsorption (macroporous structure, high ion exchange capability, small particle sizes) with the key additional advantage of a magnetic component. This greatly improves and speeds up the coagulation of the resin beads when the stirring process ceases and allows for greater recovery of the loaded resin (Bursill, 2001). Greater resin recovery reduces costs both in terms of the amount of resin required and because filters do not become clogged so rapidly, and so the MIEX resin combines the high ion exchange rates made possible by small particle sizes with easy recovery normally precluded by small particle size. The resin is regenerated through contact with brine – an extremely cheap process compared with the regeneration of GAC. The artificial resin approach therefore offers promise for improving the ability of water treatment works to continue treating highly coloured water. Whilst the MIEX resin process potentially extends the level to which water colour can be successfully treated, the upward trend in DOC levels still suggests that colour removal will become an ever greater part of treatment costs.

These "end-of-pipe" approaches to colour treatment (whereby the water is treated to the required standard at the point of use, without regard to improving the quality of the input water) have hitherto been adequate. However, if this trend of increasing colour levels was to continue then eventually a point would be reached where the water treatment works would no longer be viable (Worrall and Burt, 2005). Even before this point is reached then ever greater investment will be required in flocculation chemicals and filtration systems in order to maintain a consistent quality of output water, meaning that the point at which the treatment works is no longer economically viable may be reached even sooner.

Water companies, particularly those treating water from upland peat catchments where high colour loads are to be expected, are therefore seeking alternatives to this end-of-pipe approach to colour removal. From the point of view of water treatment, clearly a better approach would be either to prevent or to exclude the colour at source. Rather than seeking and investing in new technologies to meet the rising colour trend, there is an increasing desire to understand the underlying causes behind it and to identify the sources of increasing colour.

There is therefore a pressing need to set the causes and sources of this increasing colour trend in a spatial context such that colour production can be explained and predicted, enabling catchment managers to ensure that the water incoming for treatment is already of the best possible standard.

1.1.3 Causes of increased colour production

Peat soils have been shown (Urban et al, 1989) to be a major source of dissolved organic carbon to the drainage network, and Aitkenhead et al (1999) linked the presence of extensive peat cover in a catchment to high riverine DOC concentration. The production of dissolved organic matter in peat soil was described by McKnight et al (1985) as a microbially-driven oxidation process; that is, a process of organic matter decomposition. McDonald et al (1991) continued by describing water colour production in peat soils as a two stage process: aerobic conditions enabling greater bacterial decomposition, followed by increased wash-out upon re-wetting. This link to aerobic conditions was demonstrated for DOC by Tipping et al (1999) who linked increased DOC production to drying of the soil.

The question of why DOC concentration increases are occurring is currently an active research area. Evans et al (2005) provide a recent summary of the key potential causes; namely changes in temperature, rainfall, acid deposition, land-use, nitrogen, and CO_2 levels.

One possible reason for the increase is a general decrease in mineral acidity, following decreases in acid rain deposition. This was linked by Krug and Frink (1983) to increased DOC production, and subsequently Grieve (1990) showed a similar link when lime applications to catchments (causing increased pH) were observed to correlate with increased DOC concentrations in the stream network. More recently, Evans et al (2006) argued that decreasing mineral acid deposition, particularly decreases in sulphur deposition, together with increases in temperature, were the most likely driver for increasing DOC trends in the UK.

A second possible reason for the increase in DOC concentration is through changes in hydrology, particularly introduced through changing patterns of rainfall. Burt et al (1998) note a trend in UK rainfall patterns towards wetter winters and drier summers, and Osborn and Hulme (2002) found that the wetter winters were particularly manifested by an increase in heavy rainfall events. In the context of a relationship between water table drawdown or drought periods and increased DOC export (discussed below) the drier summers may lead to increased DOC export in the autumn rewetting period (e.g. Mitchell and McDonald, 1992; Scott et al, 1998). However, the relationship between DOC concentration and DOC export, which is also dependent on changes in flow patterns, is less clear. Forsberg (1992) found that increased precipitation was responsible for the majority of increases in DOC export into several Swedish lakes, but Tranvik and Jansson (2002) show that changes in the annual cycle of precipitation may be important. Tranvik and Jansson (2002) showed that decreasing precipitation may decrease overall DOC export, as decreasing discharge leads to longer retention times in lakes, allowing greater DOC removal, but equally that decreased discharge will cause increased DOC concentration in the soil runoff. Therefore although decreasing precipitation may lead to decreased DOC export from a catchment, this will depend on the scale of the system and effect on the overall hydrology of the system.

A third possible reason for the increases is through increases in temperature. Freeman et al (2001a) connected the increases in DOC that they observed with rising atmospheric and peat temperature, due to increases in the activity of the phenol oxidase enzyme at higher temperatures – phenol oxidase itself was shown by Freeman et al (2004) to have a key role in increasing DOC production as the phenolic compounds it removes are themselves responsible for inhibiting the activity of hydrolase enzymes involved in decomposition. Worrall et al (2003a) also observed a correlation with temperature and linked this to an increase in microbial decomposition of peat. Tipping et al (1999) demonstrated this directly by transporting peat cores to warmer, drier locations and observing a subsequent increase in the production of dissolved organic matter relative to control sites. Furthermore, temperature may play a role through increased faunal activity, particularly that of enchytraeid worms, the activity of which is strongly related to DOC concentration (Cole et al, 2002).

Analyses of long term records of DOC export show clear positive correlation between periods of water table drawdown and subsequent increased export (e.g. Naden and McDonald, 1989). This is due to the nature of the production of DOC from organic soils. Freeman et al, (2001b) proposed the theory of an "enzyme latch" mechanism by which colour production is understood not simply as an aerobic process, but rather as one where hydrolase enzymes responsible for decomposition and DOC production are inhibited by the presence of phenolic compounds. These build up under anaerobic conditions because the activity of the phenol oxidase enzyme is inhibited in the absence of oxygen. Given a period of water table drawdown, leading to previously anaerobic conditions becoming temporarily aerobic, the action of phenol oxidase is increased and these repressive phenolic compounds are removed. Activity of hydrolase enzymes can then increase (Freeman et al 2004), enabling greater DOC production which can continue even following water table restoration and the return of anaerobic conditions. This theory implies that water table fluctuations can potentially have a large effect on DOC export, which may extend for several years after restoration of the water table. Several studies since have found evidence to back up the theory and suggest that this is indeed the case, for example Worrall et al (2004b).

In summary, increased temperature may lead to increased DOC production directly through increased microbial and faunal activity, through lowering of water tables leading to increased oxidation, and – combining these factors – through an "enzyme latch" mechanism which also encourages step changes in production that do not quickly return to prior levels. It is therefore proposed that land management strategies which result in a lowering of the water table in peatlands may be implicated in the increased colour production; the key such management strategy is peatland drainage or gripping.

1.2 Background to peatland drainage

1.2.1 Peatland management

For decades upland peat moorlands in the UK have been managed as a major part of the rural economy in the areas throughout which they are found. Key goals, as with any land-based economy, have been to maximise the economic potential of the land. Blanket peatland is largely unsuitable for cropping and so the main farming in these areas has traditionally been sheep grazing. In addition the habitat is also that of grouse and other game birds, which has led to the development of large estates where the main economic use of the areas is as grouse moors for shooting and sport.

This has led to a system whereby many areas of peatlands are managed by a team, often employed by the estate to whom the land belongs, from permanent estate managers through to beaters and temporary staff employed during the busy shooting periods. Areas that may appear to be bleak wilderness are in fact managed extremely closely on a day to day basis by these teams to maintain the habitat in the optimum condition for the grouse and sheep, both of which have specific requirements such as sufficient new, edible, shoots of heather, and areas which are not entirely waterlogged. Techniques for this have been developed and refined over time - varying of grazing patterns and areas in which in grouse are bred and shot in any particular year; burning areas of heather on a suitable timescale to encourage sufficient regrowth without damaging the underlying ecology; and in recent decades modifying the natural drainage of the peatlands. The purpose of this work is to study the effect of these drainage modifications on the DOC export of the drained catchments.

1.2.2 Rationale for and problems with drainage

One of the perceived problems in peatland management has been insufficient drainage in many areas, especially large, relatively flat areas of blanket peat. The hydraulic conductivity of blanket peat can vary greatly (Rycroft et al 1975) and is much higher in the topmost, aerobic layer than in the underlying permanently saturated layers. This gives rise to a two-layered or "diplotelmic" model of peat behaviour with the layers being known respectively as the acrotelm and catotelm (Ingram, 1978). The acrotelm is the region within which the water table fluctuates and along with higher hydraulic conductivity has a greater density of microorganisms and living plant material (Holden and Burt, 2003a). Particularly in flatter areas where lateral drainage is slower due to the lack of slope, the water table can often be at or extremely near to the surface and the acrotelm is thin. The lower layers remain waterlogged, with the associated much lower catotelmic hydraulic conductivity of the order of 10^{-7} cm s^{-1} (Holden and Burt, 2003b).

Sheep in particular were observed to be affected by the waterlogged surface, as they avoid areas that are entirely waterlogged and "boggy" with the water table at or near to the surface; they become vulnerable to conditions such as footrot in the absence of dry land. In addition these conditions encourage in particular the growth of *Sphagnum spp.* over the other major habitat flora, *Eriophorum vaginatum* and *Calluna vulgaris* which provide food for sheep, and food and shelter for grouse respectively. Furthermore, waterlogged boggy ground is less suitable for the most profitable activity to take place on the land – grouse shooting. Grouse shooting requires ready access to the land by substantial teams of people, animals, and often vehicles. This is much less practical to achieve, and less desirable for the paying customers of the shoot, in areas of sphagnum bog than it is on heather moorland. Thereby draining was perceived to improve land for grouse shooting both through improvement of the habitat for grouse through increased heather growth, and through improved access.

The advent and ready availability of mechanical diggers and the development of the Cuthbertson plough in the 1930s encouraged the development of extensive networks of drainage ditches, also known as grips, across large areas of blanket peat moorland in response to government grants for "improvement" of the land for forestry and agriculture (SNH, 2006; Holden et al, 2004). The aim of the process of gripping was to improve the land for grazing, game, agriculture and access (Ratcliffe and Oswald, 1988). The process of gripping was conceived to increase the runoff from the upper layers of peat, as a lateral drainage path is made available into the side wall of the grip, thus lowering the water table around the grip. Ratcliffe and Oswald (1988) estimated that, of the approximately 8% of the UK that is covered by blanket peat moorland, approximately 75% has been gripped.

When dug, the grips are largely uniform (due to the use of the standard Cuthbertson plough) in having a trapezoidal cross-section, 50cm deep, 90cm broad at the top, and 40cm broad at the base. Grip networks vary from a few grips whose primary purpose was to modify an existing natural drainage pattern or reduce erosion, to extensive networks of grips of a branching or herringbone structure, where spacing between grips can be as little as 7m – with typical spacings traditionally being of the order of 1 chain (20m) apart.

However, despite the aims of drainage, Watson and O'Hare (1979) found no evidence for increased grouse numbers on drained bog, and indeed over the last decade there has been an increasing feeling among land managers and other stakeholders that the grip networks are not an unqualified success in providing the benefits for which they were intended. Even prior to this shift, Stewart and Lance (1983) found no documented evidence of any actual economic benefits from drainage. The failure of drainage programmes to achieve the desired results is manifested in two main ways.

Firstly, dense grip networks cause problems in themselves. From the point of view of grazing, sheep will avoid areas criss-crossed by numerous grips which, at 90cm wide, are to them substantial obstacles. Grazing patterns therefore change and sheep become harder to herd and manage. Sheep prefer drier land, which is likely to occur close to the grip channels and in particular on top of the ridge of peat spoil left alongside the channel by the plough. However a tendency by sheep to congregate in these linear patterns will only cause greater erosion at the grip edges, increasing waterlogging once again (Stewart and Lance, 1983). Grips at their originally dug size can pose a danger to lambs, and grips that have become wider and deeper through erosion can even trap adult sheep, especially where heather growth overhangs the edge of the grip (Stewart and Lance, 1983; Thompson, 1948). Similarly for grouse, grips cause a problem especially during the vital nesting season (Phillips and Moss, 1977).

Flightless chicks often fall into grips and at this stage in their lives they are not waterproofed. They are therefore unable to escape and usually drown. In densely gripped areas this substantially reduces yields.

Secondly, grips are often not successful at lowering the water table to a useful extent other than in the immediate vicinity of the grip, meaning that an extremely dense grip network is required in order to reduce the waterlogging of the land to the extent desired. This effect is discussed more fully in section 1.2.4.

1.2.3 Context of peat drainage outside the UK

Drainage of peatland is also widespread outside the UK (Holden et al, 2004) – Joosten (1997) states that approximately 60% of European peatlands have been altered through processes such as drainage. However, the reasons for drainage differ – peatlands are rarely managed for game outside the UK, but drainage is undertaken to alter peatland hydrology, to improve the suitability of peats for forestry or agriculture, or prior to harvesting of the peat. For example, Stephens and Symons (1956) describe a shift in the rationale for drainage in Ireland from flood reduction to a need for increased productivity in upland farms. Bowler (1980) reports extensive drainage with similar aims in New Zealand. Cooper et al (1991) stated that in Northern Ireland only 169km^2 of a total 1190km^2 of peat were undrained. In Finland, where drainage is undertaken chiefly to lower water tables to enable afforestation, necessitating very dense drainage networks (Holden et al, 2004), 57,000km^2 of peatland have been drained since the 1930s (Laiho et al, 1998; Joensuu et al, 2002).

In other parts of the world, drainage has been shown to have serious environmental consequences: a recent report by DELFT Hydraulics and Wetlands International (Hooijer et al, 2006) describes the extent of peatland drainage and burning in Indonesia, where a key and increasing motivation for drainage is the use of land for the production of bio-fuels. Of 210,000km^2 of peatland in Indonesia, 90,000km^2 are currently drained. The decomposition of peat caused by this leads to annual CO_2 emissions from peat degradation, in

Indonesia alone, of around 2000 Mt – this is approximately one third of the total annual CO_2 emissions of the USA (Hooijer et al, 2006). These figures suggest that producing biofuels on drained peatland can lead to the overall CO_2 emission of the biofuel being 10 times greater than that of the same quantity of fossil fuel.

Peatland protection and restoration programmes are also widespread in several countries outside the UK, such as Ireland (Dáil Éireann, 1998), Canada (e,g, Waddington and Price, 2000), Estonia, Sweden and Finland (Vasander et al, 2003). However, the magnitude of drainage such as that described by Hooijer et al (2006), together with current biofuel subsidies, mean that globally the effects of new drainage seem likely to greatly outweigh those of current peat restoration projects

1.2.4 Hydrological effects of drainage

The key expected and desired effect of peatland drainage in the UK was to lower the water table in the peat, resulting in a "firmer" surface more suitable for grazing, walking and other access. However due to the low hydraulic conductivity of peats and the often low relief of the areas over which they are found, the water table is generally not found to drop in the manner which was originally desired (Stewart and Lance, 1991).

Studies dating back as far as the eighteenth century have suggested that peatlands store water in a similar manner to a sponge, soaking up water during storms and releasing it gradually over a significant period of time, thereby reducing flood peaks and sustaining baseflows (Turner, 1757). However the opposing view has been demonstrated by many more recent studies, showing that the water table rarely drops far enough in blanket peats that substantial storage capacity is available to attenuate flood peaks (e.g. Eggelsmann, 1971). This supports observational data that blanket peats produce a great deal of runoff with extremely flashy hydrographs and relatively small baseflow contributions (for example, Burt et al, 1990; Burt et al, 1997; Evans et al, 1999).

A flashy hydrograph may seem to suggest that waterlogged peats can easily be made to give up their water and that drainage should be successful, probably adding further to the flashy nature of the hydrograph response. However many studies have shown that the vast majority of flow in peats takes place over the surface and through the upper few cm (e.g. Holden and Burt, 2003b; Ingram, 1967; Rycroft et al., 1975). Drainage may well play a part in increasing the flashy nature of the hydrograph response, by increasing surface runoff as overland flow has only to travel as far as the nearest drain channel before it is rapidly removed, with flow in drains being even faster than flow over the peat surface or through the near surface layers. However the implication of this near-surface dominated flow is also that the water table drawdown caused by a grip may not extend a great distance laterally from the grip. Any drop in the water table caused by lateral flow from the lower peat layers into the side walls of a drain channel will be slow enough that it is easily replenished by infiltration from above. Silins and Rothwell (1998) also made the point that drainage is likely to lead to some subsidence and compaction of the peat layers, which will decrease hydraulic conductivity and increase water retention, acting against the aim of drainage by limiting flow of water into the drain channels.

Any lowering of the water table by drains may cause additional carbon production. Increased soil CO_2 respiration has been observed upon drainage of peatlands by Silvola et al (1985), and Komulainen et al (1999) showed that the soil respiration of CO_2 decreased following restoration of the water table at a peatland in Finland. Methane exhibits the opposite behaviour: Tuittila et al (2000) have shown that upon restoring a cut-away peatland there was a significant increase in CH_4 flux. With respect to DOC Clausen (1980) found that concentrations increased upon drainage, and Mitchell and McDonald (1995) showed that at a catchment scale, the most densely drained areas were the largest sources of DOC.

Overall then, the likely effect of drainage seems to be to increase the flashy nature of the hydrograph response, chiefly from a relatively narrow zone either side of the drains in which the water table is lowered, while not lowering the water table enough over the peatland as a whole to gain the intended benefits

(Stewart and Lance, 1991). The reasons for increased DOC export following drainage – either due to hydrological changes, or to increased production through a mechanism such as the enzyme latch proposal of Freeman et al (2001b) following lowering of the water table – are less clear: developing a better understanding of these is one of the aims of this thesis. This study therefore hypothesizes that drained areas are a major source of DOC within an upland catchment, and that the blocking of drains will facilitate decreases in DOC export throughout the catchment. This hypothesis implies that blocking of peat drainage could represent an effective management strategy that would decrease loss of carbon from drained peatlands, increase carbon storage, and mitigate the rise of DOC being experienced by water treatment works.

1.3 Aim and Objectives

The aim of this thesis to monitor and model the production and export of DOC and colour throughout the Broken Scar catchment and, in more detail, at the level of individual peat drains. Peat drainage is now believed to be generally unsuccessful in achieving the objectives for which it was intended, chiefly increased amenity value of the land by improving its quality for grazing and gamekeeping. With this in mind, and the possibility that drainage can be implicated in increased DOC export through lowering of the water table, water companies are eager for a better understanding of the likely benefits or otherwise of drain blocking programmes – how far can the increased DOC exports be attributed to drainage, and can this be remediated by blocking the drains?

By comparing blocked and unblocked peat drains, in addition to a natural stream, this study constructs detailed export budgets for a range of these small peat catchments and, by comparison of the differences in DOC export and other behaviour between the catchments, assesses the likely effect of blocking drains on DOC export. A larger scale study across the entire catchment of the River Tees above the Broken Scar water treatment works allows this to be set in the context of the sources of DOC throughout the Broken Scar catchment.

The specific objectives of the study are:

1. To conduct an intensive monitoring programme of several peat drains which have a range of management treatments, and to use the results of this programme to create detailed DOC export budgets for the drains

2. To examine the differences in behaviour between the drains and determine to what extent such differences are due to blocking

3. To identify key source areas of water colour throughout the catchment of the River Tees above Broken Scar in order to describe those areas chiefly responsible for the problematic increase in water colour at Broken Scar

4. To relate the presence of such areas to their spatial characteristics including both catchment morphology and management techniques such as drainage
5. To review the statistical methods used in this latter form of spatial catchment modelling, and compare the results and reliability of several such statistical techniques.

1.4 Thesis outline / framework

The format of this thesis is as follows.

Chapter 2 describes and presents the results of a long-term (>2 years) campaign to monitor DOC concentration and flow in the discharge from several small peat drain catchments, with the aim of understanding the DOC export contribution of such drains through the creation of a temporally detailed discharge and concentration record. The catchments have a range of treatments – blocked drain, unblocked drain, and pristine stream – and the results are used to compile detailed DOC export budgets and compare these between the catchments.

Chapter 3 uses further monitoring and sampling of the peat drain catchments in order to identify any behavioural differences between them and further elucidate the ways in which blocking does or does not affect the export behaviour of the catchments. Several experiments are described based on several datasets: the detailed sampling campaign described in chapter 2; on additional grab-sample based monitoring; on quasi-continuous monitoring of flow and conductivity; and on a tracer flow study. The results of these experiments are used to compare differences between the catchments, with particular reference to the unblocked drain and the nearest blocked drain.

Chapter 4 describes the results of a campaign to monitor DOC concentration at a larger spatial scale, in streams around the Broken Scar catchment, and to relate this concentration to catchment characteristics such as the extent of peat cover and drainage. The results are presented using GIS mapping to compare the observed and modelled source areas and, through the use of logistic regression models, to identify specifically those areas which contribute to observed water colour at Broken Scar. This work extends the results of several previous studies, and as such the modelling is conducted in the context of a comparison of the validity of various statistical techniques which are used in this and other studies to model colour export from spatial characteristics.

Chapter 5 assesses the mixing of waters throughout the Broken Scar catchment using multivariate analysis techniques and based on the same grab sampling campaigns described in chapter 4. This is done in order to identify the sources of different types or end-members of water, with particular relevance to high colour water, enabling a different approach to the spatial mapping of colour sources.

Chapter 6 presents the conclusions of the work. The conclusions of the previous chapters are summarised and the links between the results of the two main monitoring scales are discussed. The relevance of the results in context of the water treatment works at Broken Scar is described and suggestions for further investigations are presented.

2 DOC Budgets of small peat catchments

2.1 Introduction

This chapter describes a study that was conducted with the aim of monitoring in detail the export behaviour of five small peatland catchments, in order to construct budgets for the dissolved organic carbon export of each catchment. The catchments are all situated in blanket peat and are distributed across three sites in the North Pennines, England. The first three catchments are adjacent and located on Hexhamshire Common, within the Strathmore Estate above the village of Allenheads in the Derwent Valley, at grid reference (NY869475). The other two catchments are located approximately 2 km from each other and approximately 17 km SSW of the Hexhamshire Common site, on the north and east shores of Cowgreen Reservoir, Teesdale, at grid references NY802317 and NY818304 respectively. Location of the sites within the UK is shown in Figure 2.1. The sites were selected to represent a range of drainage treatments: four are artificial drains and the fifth is a pristine peatland stream. Of the drained catchments, one was blocked in 1995, two were blocked at the outset of this study, and one remains unblocked. Data were also obtained for a larger peatland stream catchment.

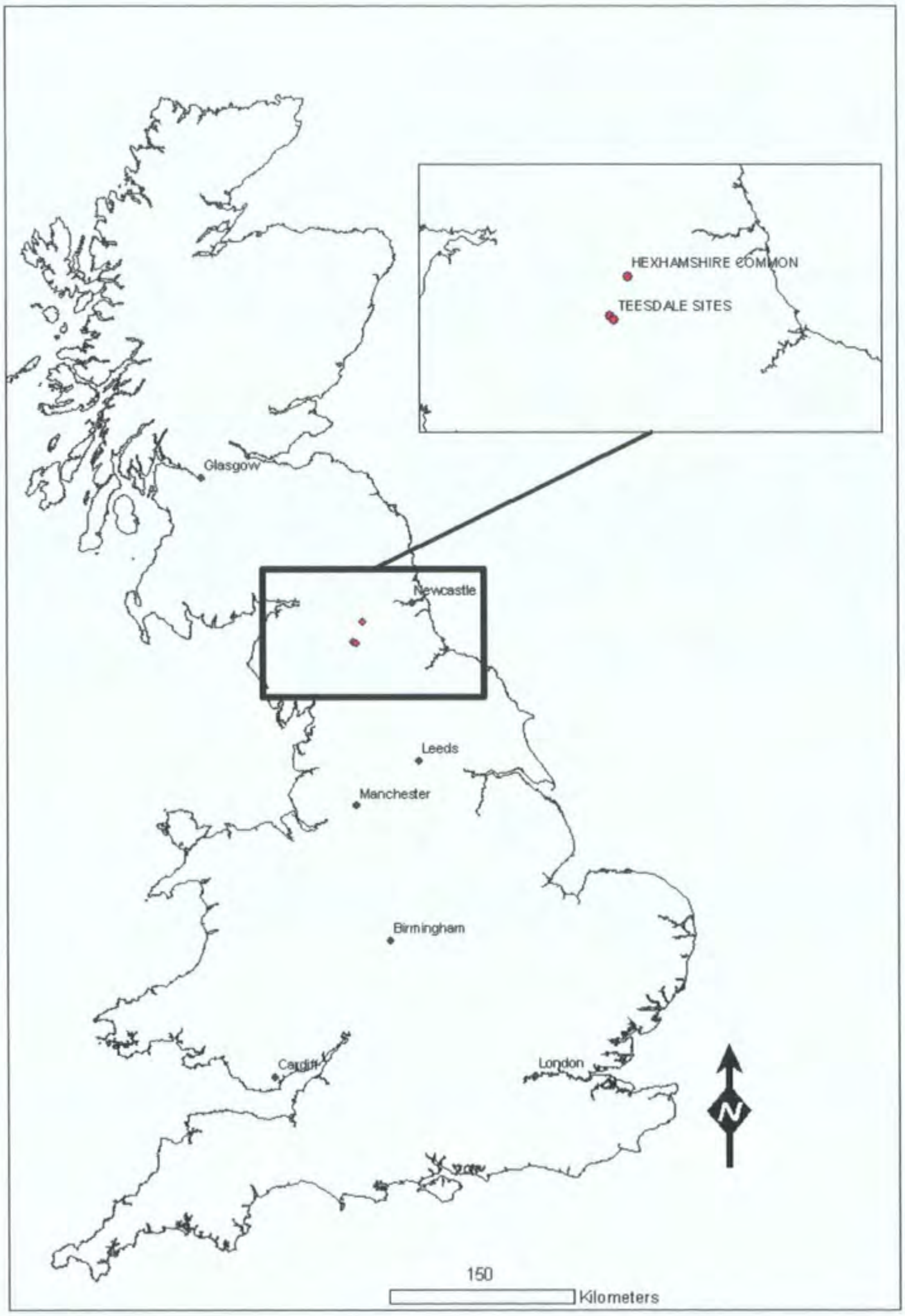


Figure 2.1 Location of the study sites. Data source © Crown Copyright/database right 2005. An Ordnance Survey/EDINA supplied service

2.1.1 Restoration of drained peat

The purpose of this chapter is to develop an understanding of the effect of drainage on the DOC exported from peatlands. As described in chapter 1, peatland drainage has been implicated as one possible cause of the increasing trends in colour and DOC export observed in many peatland rivers. Drainage has also been shown to increase the concentrations of many solutes, including Ca_2^+, Mg_2^+, Na^+, NH_4^+, and conductivity (Prevost et al, 1999).

One potential method of reversing the effects of drainage is to block the grips. Several different methods are used for blocking grips. Dams made of imported materials such as plastic or wood can be extremely effective and reduce mean flow velocity by as much as three orders of magnitude (Holden et al, 2005). Dams may alternatively be made of locally available materials such as bales of heather, or blocks of peat cut from areas between grips (known as the "cut-and-shut" method). Such dams are somewhat less effective but can still reduce mean flow velocity by two orders of magnitude compared to open drains (Holden et al, 2005). Filling-in of the entire grip channel is not a common method, as it can be difficult to find sufficient material to fill in the channel without creating a new grip where the material was removed from, especially where the spoil ridge from the original digging of the grip has eroded or otherwise diminished. Whatever the construction of the dam, the much slower flow velocities generated by damming methods encourage the deposition of sediment and promote re-vegetation, which in turn helps to trap further sediment.

The aim of grip blocking has been seen as firstly, to restore the water table to pre-drainage levels, and therefore reduce DOC production; and secondly to reduce the flashy nature of the hydrograph that is caused by rapid flow through open drain channels. Focussing in particular on the first aim, this study develops a detailed assessment of the DOC export budget from small peatland catchments with a range of drainage treatments. The DOC budgets of catchments that have been managed in different ways are compared in order to test the hypothesis that the export can be reduced through a grip blocking program, and to assess the extent of such a decrease that is potentially achievable.

2.2 The Study Sites

This study has involved the detailed monitoring over a two year period of five individual moorland drainage catchments, spread across three separate sites in the North Pennines, England. All are situated in blanket peat and the catchments were selected to represent a variety of management interventions, while being geographically and physically as similar as possible.

Four are artificial catchments, which have been drained by the digging of grips at one stage. At the start of the study period, three of these catchments had open, functioning drainage, and the fourth had its drain blocked in 1995. The fifth catchment is a natural first-order stream, which is taken to represent a "pristine" catchment for the purposes of control. This site has no artificial drainage within its catchment.

The five catchments are distributed across three locations, at Hexhamshire Common, Allendale; Pikestone Hurth on the northern side of Cowgreen Reservoir, Teesdale; and Widdybank Fell on the eastern side of Cowgreen Reservoir (Figure 2.1).

In addition to the data collected for the study from these sites, data were also obtained from the UK Environmental Change Network (ECN) monitoring programme at Trout Beck in the Moor House NNR (Sykes and Lane, 1996). Trout Beck is an upland peat catchment but is significantly larger, at $11.4km^2$, than the other catchments in this study.

2.2.1 Hexhamshire Common

Three of the catchments are at the first site. This lies on Hexhamshire Common, within the Strathmore Estate above the village of Allenheads in the Derwent Valley, at grid reference NY869475 at an altitude of 520m O.D. The underlying geology is a succession of carboniferous sandstones, siltstones and limestones, and there are no apparent drift deposits underlying the peat. The vegetation of the common is dominated by *Eriophorum vaginatum*. (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum spp.* (moss) and the poor drainage has led to the development of extensive blanket peat of depths up to

2m. The field site lies within an area of the peat that has been gripped extensively and extremely densely, with grip spacing varying from the "standard" 20m (1 chain) down to as little as 7m. The three grips studied are at approximately 7m spacing. Due to the depth of the peat at this site, grips across the common are almost entirely within the peat and the grips studied are entirely within the peat: there is no contact with the underlying rock or till. The site is shown in Figure 2.2.

The grips on the common were dug in at least three phases, with the most recent being in 1995. The grips studied were dug in this most recent phase. In January and February 2003, just after the monitoring in this study began, the grips across an area of the common were blocked as part of a study by English Nature (unpublished), using a peat dam method (section 2.1.1) with peat for the dams being taken from the channel walls, causing pools upstream of the dams.

The three grips selected for this study are adjacent and approximately parallel. (Figure 2.5). Two of these, denoted Hexham 1 and Hexham 3, were blocked in the programme detailed above on the 5^{th} January 2003, using peat dams at approximately 10 metre intervals along the length of the grip channels. The remaining grip, Hexham 2, was left unblocked. The catchments of the grips Hexham 1, Hexham 2 and Hexham 3 are approximately $1800m^2$, $7500m^2$, and $2400m^2$ respectively. Hexham 2, the central grip, is significantly longer than the adjoining Hexham 1 and Hexham 3. The channel cross sections of Hexham 2 and Hexham 3 are broadly similar at the lower ends of the catchments where samping took place, in line with the dimensions produced by the Cuthbertson plough. Hexham 3 is somewhat shallower towards the upper end, above the blocks. Hexham 1 is partially filled in with sediment particularly in the lower reach, and the channel is therefore somewhat shallower than the other two grips at this site.

2.2.2 Upper Teesdale – Pikestone Hurth

Cowgreen Reservoir is a large reservoir managed by Northumbrian Water in the headwaters of the River Tees. The reservoir was created in 1971 and has an area of approximately 3 km^2. Areas around it have been gripped at varying times since the 1950s, in patterns that are generally less extensive and dense than at Hexhamshire Common. Pikestone Hurth, on the northern side of the reservoir, has been gripped with an average spacing of approximately 20m. The grip chosen for this study lies at grid reference NY802317, at an altitude of 560m O.D. The grip was blocked in 1995 using the same peat dam method that has been used more recently at the Hexhamshire Common site. The grip has partially healed in the decade since blocking and is now substantially narrower and shallower in places than the Hexhamshire Common grips. The area of the catchment is approximately 3500m^2 and the catchment is referred to in this study as Cowgreen.

Vegetation at this site is dominated by *Eriophorum vaginatum.* (cotton grass) and other grasses, and *Sphagnum spp.* (moss). There is little or no *Calluna vulgaris* (heather). The peat is underlain by a succession of limestones of the Alston and Yoredale groups, with glacial till underlying the peat deposit. The peat depth is approximately 50cm. This is sometimes referred to as "shallow" peat, as the severest droughts would drop the water table below the peat and into the underlying glacial till, effectively cutting off the peat from the drainage system during those periods. The shallower peat means that, unlike at Hexhamshire Common, grips are sometimes cut into the underlying glacial till. However, in order to ensure maximum comparability between the sites, the grip in this study is not and is entirely within the peat. The grip is shown in Figure 2.3.

2.2.3 Upper Teesdale – Widdybank Fell

Widdybank Fell lies to the east of Cowgreen Reservoir and falls within the Moor House NNR (see section 2.2.4). The study site lies at the base of Widdybank Fell, at grid reference NY818304 and an altitude of 510m O.D. Vegetation is dominated by *Eriophorum vaginatum.* (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum spp.* (moss), and the site is underlain by limestone of the Great Scar limestone group. The site consists of a small first-order natural stream which at some points along its channel contacts the underlying limestone as well as the blanket peat. The study catchment is the south-eastern branch of the stream named on Ordnance Survey mapping as Slapestone Sike. The catchment lies entirely within the Moor House NNR, and no part of it has ever been artificially drained. The area of the catchment is approximately 27500m^2 and the site is referred to in this study as Widdybank; the stream and monitoring equipment are shown in Figure 2.4.

2.2.4 Moor House – Trout Beck

In addition to the sampling and monitoring campaigns that were conducted at the sites detailed above, flow and DOC concentration data were also obtained from the Environmental Change Network (ECN; Sykes and Lane, 1996) for the Trout Beck catchment in the Moor House National Nature Reserve (NNR). The Trout Beck (ECN 2006a) is a blanket peat catchment in the headwater of the River Tees (outlet at OS grid ref. NY758335) lying entirely within the Moor House NNR. The Moor House NNR (ECN 2006b) is both a terrestrial and freshwater site within the ECN: the ECN collects various hydrological data from the Trout Beck catchment (Sykes and Lane, 1996). The catchment lies largely above 500m O.D. with the highest point being the summit of Great Dun Fell, at 848m O.D. The underlying geology is a succession of Carboniferous limestones, sands and shales with intrusions of the doleritic whin sill (Johnson and Dunham, 1963). This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat, which covers 90% of the Trout Beck catchment (ECN, 2006a; Evans et al, 1999). The vegetation of the whole NNR is dominated by *Eriophorum vaginatum.* (Cotton grass), *Calluna Vulgaris* (heather), and *Sphagnum spp.* (moss). The area of the Trout Beck catchment above the gauging and sampling station is 11.4km^2. The mean annual temperature at Moor House (1992 – 2000) is 5.8°C and air frosts are recorded on over 100 days per year. Mean annual precipitation (1953 – 1997) is 1953mm (Burt et al, 1998) and snow forms a significant proportion of precipitation – annual average snow cover at 500m is 55 days (Archer and Stewart, 1995). Any rainfall in the catchment produces a rapid runoff response: previous studies at Moor House have shown that the lag between peak rainfall intensity and peak flow can be as little as 30 minutes (Burt et al, 1998), with a mean of 2.7 hours (Holden and Burt, 2003b).

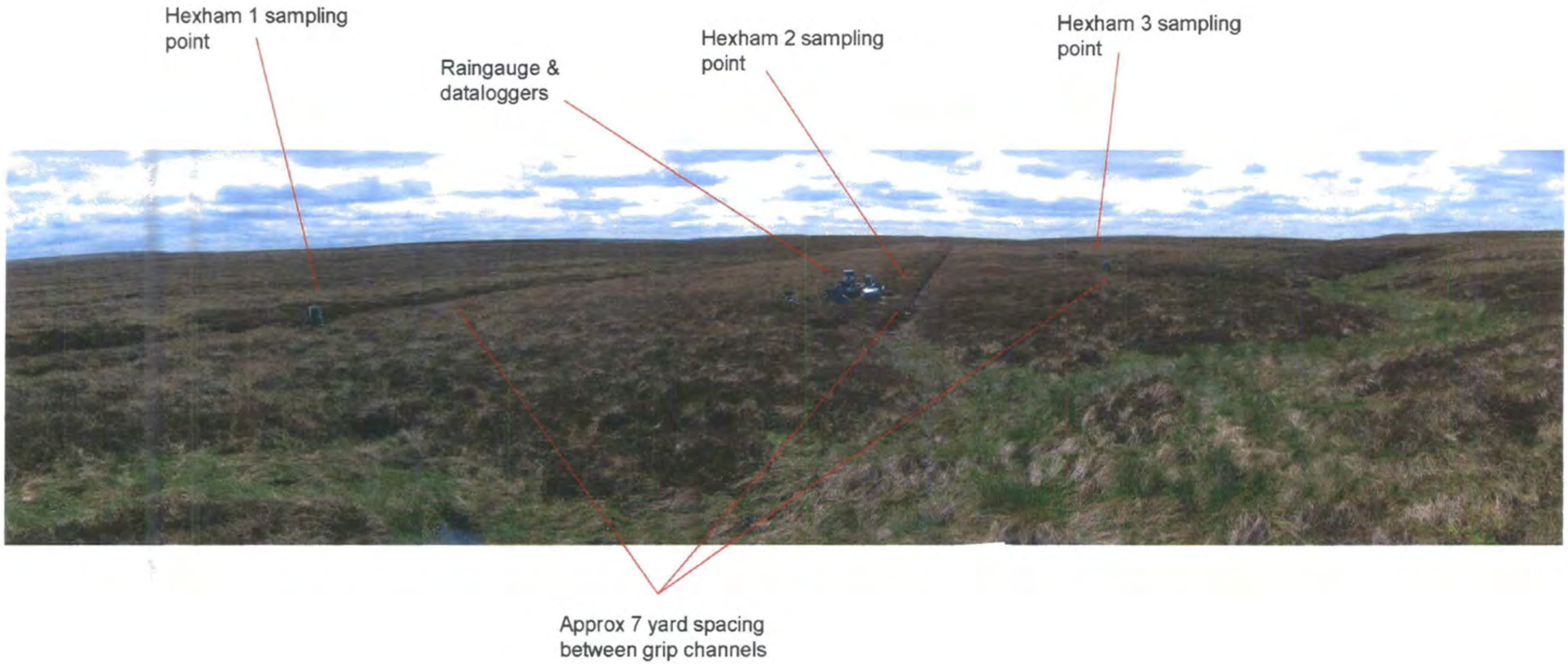


Figure 2.2 Hexhamshire Common field site

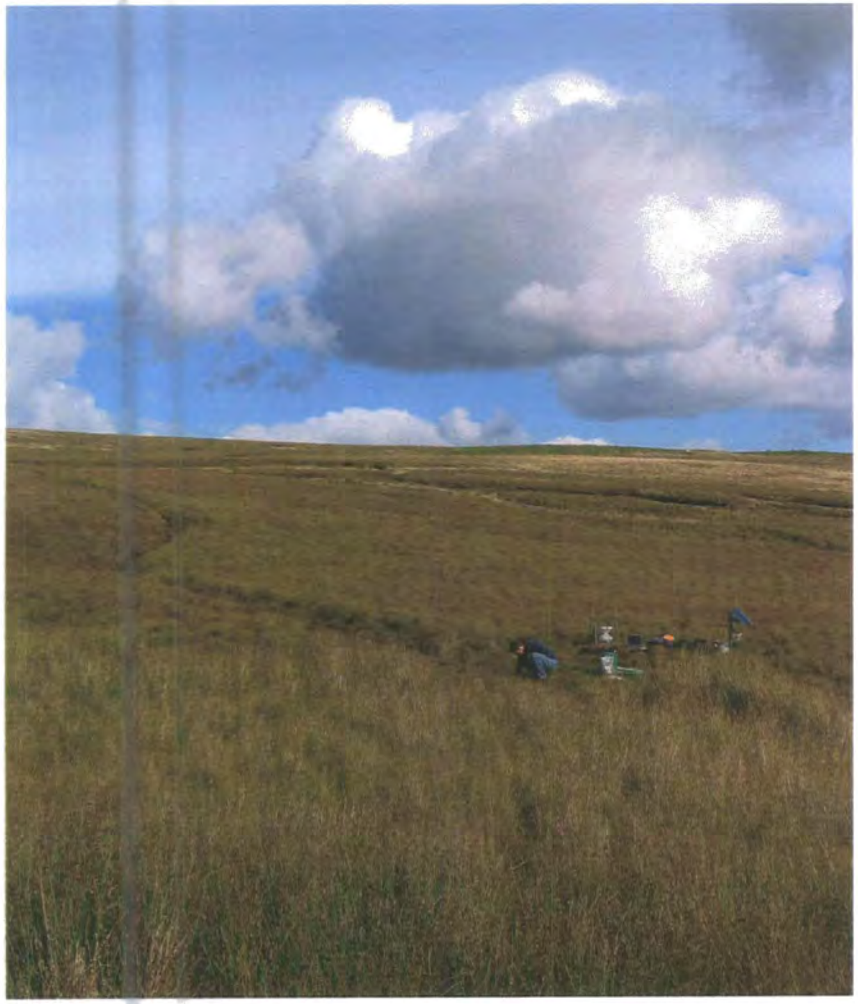


Figure 2.3 Cowgreen grip and monitoring equipment

Figure 2.4 Widdybank stream and monitoring equipment

2.3 Fieldwork programme

In order to calculate the DOC export budgets for the catchments and compare these between catchment treatment types, a detailed fieldwork programme was undertaken between November 2002 and January 2005. Few data exist on the relationship between DOC concentration and flow in very small catchments such as those in this study; developing a further understanding of this was one aim of this study. Therefore rather than attempting to develop rating curves for flow vs. DOC concentration, the fieldwork programme was designed to collect as much data as possible in order to calculate the DOC budgets directly through calculation of flow and concentration sums of products. To achieve this flow was monitored on a quasi-continuous basis using V-notch weirs with stage measurement by pressure transducers. DOC concentration was not monitored on a continuous basis (for instance by turbidity monitoring), but by frequent automatic sample collection and laboratory analysis.

2.3.1 Sampling equipment description

The outlets of the five catchments detailed in sections 2.2.1 - 2.2.3 were instrumented with automatic water samplers (Buhler-Montec Xian 1000) fitted with automatic distributors and 24 500ml sample bottles. The samplers are capable of taking samples at preset intervals, or in response to an external trigger. Samples are obtained using an indirect pneumatic pump mechanism, which reduced likelihood of equipment failure in dirty water and also reduced cross-contamination of samples as there are no locations within the sampler for a portion of a previous sample to become stuck and then mix with a subsequent sample.

The sampler was fitted with a hose of sufficient length that the sampler unit could be situated away from the stream channel to avoid the risk of it becoming flooded. The end of the hose was fitted with a brass weight to ensure the samples were taken from the base of the stream, and no filter was fitted to the hose. The hoses were carefully placed in the grips with the brass weighted end on top of a flat stone, and further weighted down by another flat stone. This was to ensure that the intake did not become stuck in and blocked by the deep soft sediment at the base of the grip. Care was also taken not to place the intake directly below the pressure transducers (see section 2.4.2) to minimise the disturbance to these caused by the sampling process.

The samples were taken by first purging the chamber and sample hose with air to remove any water stagnated in the hose from the previous sample. The direction of airflow is then reversed causing the sample to be aspirated into a fixed sample chamber, fitted with a level cut-off that serves to determine the volume of the sample as 500ml. After a preset delay the sample is then released into one of the 24 sample bottles. The fixed sample chamber and other parts of the system were regularly cleaned on site visits to minimise cross-contamination of samples.

2.3.2 Sampling frequency

For the purposes of this study samples were taken at regular preset intervals. Throughout the seasons of higher expected flow (approximately September – May) samples were taken every 8 hours where possible. During the grouse shooting season (October 12^{th} – late November) and the breeding season (mid April – early June) access to the sites was sometimes restricted. During these periods, and during the summer months (June – August) when extremely low or non-existent flow in the grips was expected for the majority of the time, samples were taken every 24 hours.

This sampling pattern was maintained throughout the period of the study with the only exceptions to the sample timing being caused by lack of access to the sites or by equipment failures. Periods when there was no water in the grips, or when the grips were frozen, also resulted in gaps in the sample record. Sampling commenced at Hexham 1, Hexham 3, and Cowgreen in September 2002 and, due to an early equipment failure, at Hexham 2 in January 2003. The Widdybank site was instrumented slightly later and sampling commenced here also in January 2003.

Sites were visited for the collection of samples usually on the day before the programmed end of the sampling run, to minimise breaks. For example, when the samples were taken every 8 hours the 24 bottles would take 8 days to become full. Therefore, the sites were visited every 7 days. This implies that samples in the storage bottles in the machine were stored for up to a week before collection throughout winter, and sometimes for up to three weeks during summer. Laboratory tests conducted in the same research group on the stability of DOC samples kept in the dark (as in the storage base of the sampler unit) and at field temperatures showed no significant change ($P<0.05$) in DOC concentration over these periods (F. Worrall, pers. comm., unpublished data).

On field site visits, samples were collected into washed 60ml containers which were first rinsed with the sample. This volume was sufficient to perform all the analyses required. Samples were transported back to the laboratory and stored in the refrigerator prior to analysis the following day.

2.3.3 Catchment delineation

For the purposes of areal DOC export calculation, the catchments of each of the grips and of the stream were delineated. In many cases moorland grips are dug approximately parallel to the contour of the slope and so the grip channel itself represents one lower boundary of the catchment. However this assumption could not be made in the case of the grip catchments in this study, as they are situated either in areas of minimal slope, in the case of the Hexhamshire grip, or running downslope, in the case of the Cowgreen grip.

Due to the flat terrain, and very small catchment size, the catchments of the Hexhamshire grips could not practically be outlined conventionally from maps or digital terrain models by using high points to estimate the watershed, as the relief of the catchments was less than the vertical resolution of the data available. The catchments of the Hexhamshire grips were therefore estimated manually in the field by assuming that each grip drained an area extending laterally halfway to the next grip in each direction. The area represented by this was marked out with a tape measure and the coordinates of the outlines produced were recorded using a differential GPS, to produce the catchment outlines as shown in Figure 2.5

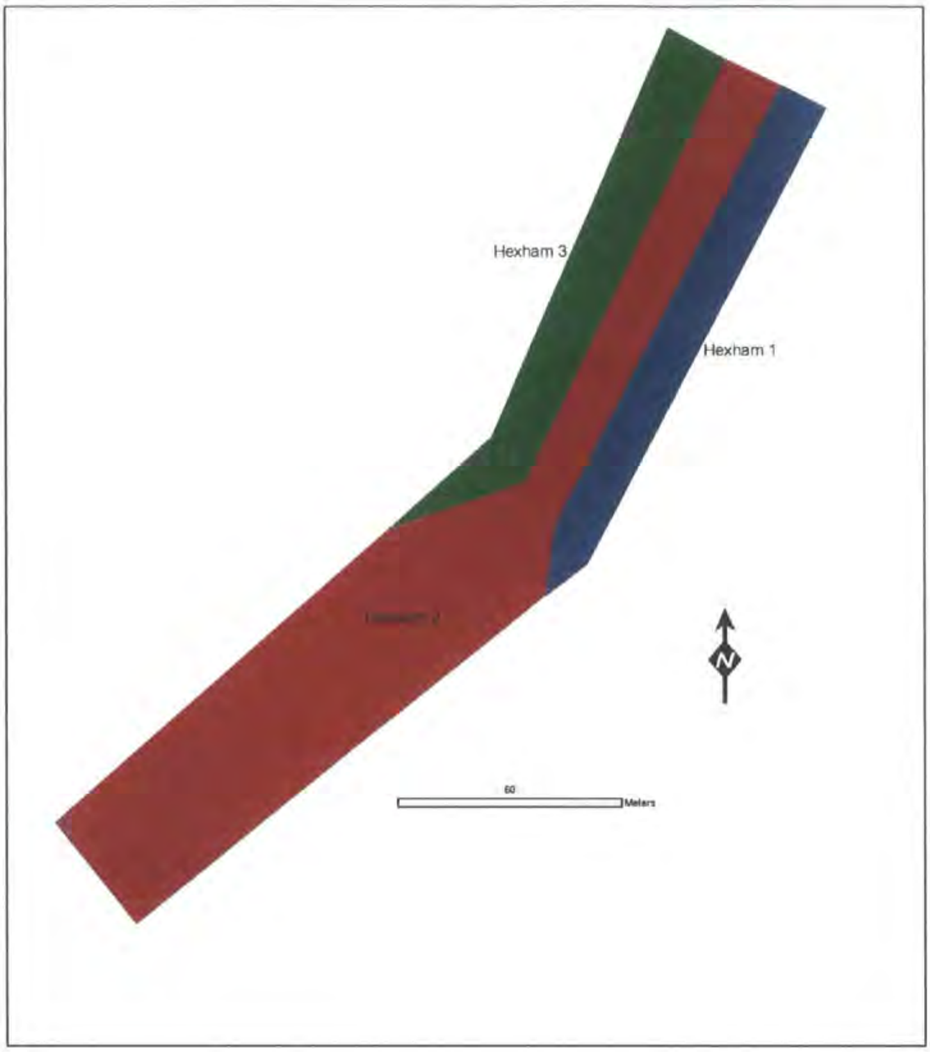


Figure 2.5 Outline diagram of the three Hexhamshire Common grip catchments

A similar process was followed at Cowgreen, however here there was significant slope which aided the process of visual catchment identification in the field.

At Widdybank Fell the catchment was large enough, and with sufficient relief, for an estimate of the catchment to be produced automatically in a GIS from a DTM (see chapter 4 for details of method). The catchment was also marked out manually in the field using a differential GPS and the results compared to the automatically-generated catchment to produce a "best estimate" for the catchment outline.

2.4 Hydrological monitoring programme

2.4.1 Flow monitoring methods

Flow was monitored from each catchment using V-notch weirs, with stage measurement via pressure transducers. The flow regime in such small peatland catchments as these was expected to be extremely flashy with peak flows being as much as two or even three orders of magnitude higher than baseflows (e.g. Evans et al, 1999). This is the case for the Trout Beck, which nevertheless has a baseflow component, and for the shallow within-peat grips in this study the baseflow will therefore be even lower in comparison to the peak flows.

Measurement of flow across such a wide range is extremely difficult. At low flows, such as the $<0.02Ls^{-1}$ experienced during dry periods in all of the grips, any errors in the measurement of stage with a weir installation become relatively more significant – such errors could be caused by inaccurate transducer installation or by suspended matter in the water blocking the lowest, narrowest portion of a V-notch and acting as a dam to raise the water level behind the weir. Under such conditions a tipping bucket would be more appropriate for flow measurement. However under storm flow conditions where flows could rapidly rise to as high as $10Ls^{-1}$, most tipping bucket systems would be overwhelmed.

Tipping buckets were also rejected as unsuitable because the water must somehow be channelled from the grip into the gauge, and then leave the gauge to drain away. This requires sufficient head to keep the water flowing through the system, and at the sites in this study this was not possible due to the relatively flat terrain. This was established as an attempt was made to augment the flow monitoring using a tipping bucket gauge (Unidata) for periods of low flow. It was found that the tipping bucket unit could not be situated below the catchment outlet point without itself being below the water table and therefore becoming flooded.

V-notch weirs were therefore selected as the best compromise, because the stage increases in less than a linear manner with increasing flow, producing as high a resolution as possible at low flows while also being capable of handling large flows.

For a V notch weir, stage is related to flow by Equation 2.1

$$Q = C_e * \frac{8}{15}\sqrt{2g} * \tan\frac{\theta}{2} h^{2.5}$$

Equation 2.1 Stage / discharge relationship for a V-notch weir

where

- C_e is the discharge coefficient for the weir, taken as
- C_e = 0.578 for the half-90° weirs
- C_e = 0.586 for the quarter-90° weirs.
- Θ is the angle of the V-notch in degrees
- g is the acceleration due to gravity, taken as 9.81ms^{-2}
- h is the depth of water over the weir in meters
- Q is discharge in m^{3}s^{-1}

Derivations of the equation are to be found in ISO(1980) and a summary is available in LMNO(1999).

Weirs were selected to match the expected comparative flow from each catchment based on their size: the largest catchments, Widdybank Fell and Hexham 2 were instrumented with half-90 weirs (notch angle = 53.1°) and the remaining catchments with quarter-90 weirs (notch angle = 28.1°). The terms half-90 and quarter-90 refer to the flow produced at a given stage being half and quarter of that produced by a 90 degree weir at the same stage. That is, $\tan\frac{\theta}{2}$ for a quarter-90 weir is half that for a half-90 weir.

The weirs were constructed from marine plywood and installed across the grips such as to extend at least 30cm beyond the sides and bottom of the grips, to eliminate bypassing flow.

Flow data was obtained for the Trout Beck catchment from the ongoing ECN monitoring programme. Flow was measured at a compound crump weir; meteorological parameters including rainfall and air temperature were also obtained from the ECN monitoring programme (Sykes and Lane, 1996).

2.4.2 Stage Measurement

Stage measurement was achieved in the grips using pressure transducers to sense water depth, and calibrating the sensed depth to water head over the weir. Pressure transducers (Druck PDCR1830, approx 2mm resolution, details at Druck (2004)) were fixed directly to the back of the weir plates. The transducers were fixed towards the side of the plate and away from the notch, in order that they were in relatively still water and away from the depression in the water column as it flowed out of the notch. Transducers were connected to the dataloggers (CR10X, Campbell Scientific, details at Campbell (2006)) using a four wire technique. The six wire technique, which corrects for the variation of the resistance of the cable with temperature, is only necessary with longer cable lengths than were used, and measurements made with the four-wire technique were found to be well temperature compensated. All transducers were sampled every 10 seconds with the average reading being recorded every 15 minutes.

Dataloggers were each powered by a 7Ah lead-acid battery with backup power and trickle charge to the batteries provided by solar panels, ensuring that the dataloggers could run without interruption even where visits to the site were precluded for the reasons discussed in section 2.3.2. The datalogger memory was sufficient to store at least 6 weeks of data ensuring that no data was missed where site visits were infrequent. On field visits data were downloaded to a portable PC using the Campbell Scientific PC200W software.

Pressure transducers work by sensing changes in the electrical resistance of a quartz crystal under varying pressure. The PDCR1830 transducers used were of millivolt output type, whereby the transducer is supplied by the datalogger with a regulated excitation voltage, and the output voltage, as a proportion of the excitation voltage, varies in a manner that is ratiometric to the pressure. The dataloggers were programmed to supply a 10v excitation, at which voltage the full scale output of the transducers was 50mV.

This change in the output voltage of the pressure-sensing element is also dependent on temperature and so accurate temperature compensation is required. The Druck transducers are well compensated against temperature change using a factory-set routine built into the transducer circuitry. No further compensation was found necessary as minimal correspondence was observed between the transducer readings and water temperature. To correct for any drift in the transducers and error in the weir calibration constants, manual flow measurements were taken on field visits where flow was high enough to measure accurately, by directing the flow into a container of known volume and measuring the time taken to fill this. The effective actual weir head required to produce this flow could then be calculated from Equation 2.1, and this actual head compared to the transducer reading at that time.

The PDCR1830 transducers are vented, so pressure measurements were of relative (gauge) pressure and therefore not affected by fluctuations in atmospheric pressure.

Transducer measurement with the PDCR1830 transducers proved largely accurate and reliable while the weather conditions allowed them to operate within their specified conditions. However problems were experienced in winter when the grips froze. If the grips froze deeply enough to reach the transducer then this would lead to an extreme rise in pressure at the sensor head as ice around the transducer expanded. This phenomenon damaged several transducers and is the main cause of gaps in the data, especially since the damage tended to happen at times when field site visits were precluded due to the weather, meaning the damage was not immediately discovered or remedied. Other data gaps were caused, especially at the Cowgreen site, when transducers suffered damage through wildlife such as rabbits and sheep gnawing through the cables.

In March 2004 the transducers in the Hexham 1 and Hexham 3 grips failed. They were replaced with pressure transducers from Intelisys Ltd which were connected to a Sentry II datalogger, produced by the same company. A third Intelisys transducer was also installed in the Hexham 2 grip, alongside the remaining functional Druck transducer. The Intelisys transducers operate on the same principle as the Druck PDCR1830s and are also fully vented. (These transducers are now discontinued and the company defunct; however details of the datalogger are available at Salamander (2006).)

This change of equipment was due to a lack of spare Druck transducers and the desire to find a system that was more robust against freezing. However, the Intelisys system did not prove to be an entirely satisfactory alternative. Due to limitations with the Sentry II datalogger, the Intelisys transducers were sampled only every 15 minutes: the 15-minute data recorded therefore represent individual transducer samples rather than average readings over the 15 minute period. This leads to a somewhat noisier record that required more manual processing to eliminate inaccuracies. Additionally, the factory-set temperature compensation in the Intelisys transducers proved to be entirely insufficient, with strong correlations being observed between temperature and transducer output that were not explained by actual fluctuations in the water level as measured manually or via the Druck transducer, and which could not be entirely filtered out from the data. Furthermore, gaps in the data from the Intelisys transducers were caused by premature failure of the datalogger power supply.

2.4.3 Flow modelling

The various gaps in the flow record caused by equipment problems, together with the poor quality of the data from the Intelisys systems, meant that for the Hexham 1, Hexham 3, and Cowgreen sites in particular the DOC export budgets could not be calculated for the entire period from the recorded data. However, good rainfall data was available for the whole study period for the Hexhamshire site and so to reconstruct the flow record where necessary, rainfall-runoff models were constructed for each site using an extension of the unit hydrograph method. For the Cowgreen site, the rainfall record itself was partially reconstructed from the record of a neighbouring site, before using this to reconstruct the flow record as for the Hexhamshire sites.

Jakeman and Hornberger (1993) provide an analysis of the accuracy of rainfall-runoff modelling and conclude that once actual rainfall is converted into "effective" rainfall (based on a non-linear loss function accounting for factors such as varying evaporation), the rainfall-runoff response of a wide range of catchments can be accurately represented by relatively simple models without the need for more complex parameter optimisation. This supports the use of the unit-hydrograph method over more complex techniques which seek to take account of details such as catchment terrain and vegetation properties.

2.4.3.1 Unit Hydrograph Method

The basic assumption of the unit hydrograph method is that for a given catchment, a normalised "unit" of rainfall, for example 1mm, falling over a fixed time period, for example 15 minutes, will produce a single and predictable hydrograph pattern known as the unit hydrograph. For a given catchment, this unit hydrograph is established empirically by selection and analysis of suitable storms in the rainfall-runoff record.

Once the unit hydrograph for the catchment is known, the hydrograph resulting from a particular storm event can be estimated by superimposing the unit hydrograph in the same way that the rainfall produced by that storm is a superposition of a unit rainfall. For example, 2 units of rain falling over one unit of time is assumed to produce a hydrograph with ordinates twice as large as those of the unit hydrograph, whilst a unit of rain falling in each of two subsequent time units produces a hydrograph that is given by summing the ordinates of two unit hydrographs starting one time unit apart.

For each site, the Unit Hydrograph method was applied manually in an attempt to calibrate the rainfall-runoff relationship, by identification of storms and comparison to runoff hydrographs to construct the unit hydrographs. However this approach met with limited success as the unit hydrograph developed for any one part of the catchment record was found to produce very poor predictions of runoff at other times. It seems likely that for such small catchments the non-linearity between rainfall and streamflow, due to the effect of temperature and associated evapotranspiration rate changes, cannot be neglected as is assumed by the unit hydrograph approach. Therefore results from this direct approach are not discussed further.

2.4.3.2 IHACRES Model

A more sophisticated approach was taken by extending the unit hydrograph approach to include losses due to evaporation. The software package IHACRES (**I**dentification of unit **H**ydrographs **A**nd **C**omponent flows from **R**ainfall, **E**vaporation and **S**treamflow) was adopted for this modelling. The IHACRES software consists of a PC based package (Littlewood et al, 1997; Jakeman et al, 1991) which was subsequently extended into a Java-based implementation (Croke et al, 2006). The latter version was used in the present study as it provides greater facility for searching and comparing different model calibration parameters. The IHACRES model enables rainfall-runoff modelling which is based on the unit hydrograph method, but the model is extended to include evapotranspirative water losses from the catchment.

The system has two main parts or modules: a non-linear loss module, and a linear module. In the non-linear loss module, actual rainfall from the input record is converted to an effective rainfall (the portion of rainfall that actually contributes to runoff), by taking account of evapotranspirative losses and current catchment wetness. This module takes temperature data (or direct evapotranspiration data) for input, and the model is then calibrated to determine the relationship between rainfall, potential evapotranspiration, and effective rainfall for that catchment. Once calibrated, the effective rainfall rather than the actual rainfall is then passed to the linear module which models effective rainfall against runoff using the unit hydrograph principle.

This method proved vastly more successful than a simple unit hydrograph approach for modelling the rainfall-runoff relationship of the catchments in this study. The catchment with the most complete existing runoff record was

Hexham 2, so the IHACRES system was tested initially on the records from this catchment, as the model could be calibrated and then validated successfully and more extensively than was possible in the other grip catchments. Once the efficacy of the method had been established, models were also developed for the other catchments and used to fill in the gaps in the runoff record.

Due to limitations of the modelling software, the model could not be successfully run to predict flow on the 15-minute timestep of the original data. Therefore the flow, temperature and rainfall records were first aggregated from the 15-minute data to 6-hour data, with mean values for flow and temperature and total values for rain being taken for each 6 hour period. This approach is justified as the DOC sample data with which the flow values were multiplied for export calculations was never more frequent than 8-hourly and so little additional inaccuracy was introduced by this aggregation, as discussed further in section 2.6.1. To check this assumption, export budgets were also calculated for the Hexham 2 and Widdybank catchments from the original 15-minute data in addition to the 6-hour aggregated observed record, for periods of continuous good data; this enabled comparison of the budgets calculated from each timestep to identify any loss of accuracy in the coarser data.

The non-linear loss module of the IHACRES model is calibrated using 5 related parameters:

- Catchment drying rate at reference temperature (T_w)
- Temperature dependence of drying rate (f)
- Reference temperature (T_{ref})
- Moisture threshold for producing flow (l)
- Power on soil moisture (p)

Once a calibration period in the data record has been selected, suitable values for these parameters are found by empirically searching through a matrix of possible values, and testing the efficiency of the resulting models for each combination of parameter values. Further details of the parameter selections that were made for each catchment are presented in section 2.7.1.

The linear (unit hydrograph) model has only two configuration options:

- Delay between peak rainfall and peak flow
- The physical store configuration of the catchment

For all the catchments, the best value for the delay was found to be 0 model timesteps; that is less than 6 hours. For catchments of this size, this is as expected as peak flow does not lag peak rainfall by more than 6 hours. Indeed, for the much larger peatland catchment of the Trout Beck in the Moor House NNR, the lag has been shown to be as little as 30 minutes (Burt et al, 1998) and therefore it seems reasonable to accept that the lag in each of these much smaller drain catchments would be shorter.

The physical store configuration of the catchment refers to the way in which the model assumes water is stored in and released from the catchment, in terms of the relative contributions of quickflow and baseflow. All of the grip catchments are observed and expected to have little or no baseflow component to the flow, and so the model was set up with the catchments each represented as a single exponential store. If the catchment structure was represented as having quickflow and baseflow components, it was found that the model could not be successfully calibrated for any of the drain catchments, confirming that no significant baseflow component could be identified in the flow data. The Widdybank catchment was modelled using a two parallel store structure, representing a significant observed baseflow component to this catchment.

2.5 Sample Analysis

Samples were analysed both for DOC content to calculate DOC export, and for other characteristics to assess character of the source (data from these additional analyses are presented in Chapter 3). Due to the large number of samples produced each week during the study, actual DOC was measured only on a subset of samples from each site, using the colorimetric method of Bartlett and Ross (1988). Absorbance, being quicker to determine, was measured on every sample and for each site a regression fit was developed between absorbance at 400nm and DOC content (Hautala et al, 1999). This regression was used to calculate DOC content for each sample from the absorbance measurements.

2.5.1 Sample preparation

The analysis of samples, both for absorbance and for colourimetric determination of DOC concentration, was conducted on unfiltered samples. Although in contrast to the most common protocol, this approach was deemed acceptable for several reasons. Firstly, all samples remained in the autosampler bottles for periods ranging from several hours to one week prior to collection, and on collection the 50ml subsample was carefully decanted to avoid disturbing the settled sediment. Prior to laboratory analysis, these 50ml vials were stored upright for 24-48 hours and the sample was transferred to the cuvettes using a pipette placed in the uppermost portion of the container. This double decanting ensured minimal sediment in the aliquots. Secondly, a number of samples were filtered to 0.45μm as part of a separate experiment (not included in this study). The results of this indicated only a slight decrease in absorbance following filtration, of the order of 10%, and Hope et al (1997a) found the decrease in apparent DOC measured following filtration to differ by less than 5% from unfiltered samples. Finally, the colourimetric method used for DOC determination is affected only by dissolved carbon – any present as particles will not contribute to the reaction. With all these reasons taken into consideration, the much greater number of samples that could be analysed without filtration, and the more detailed DOC budgets thus produced, was deemed to be more beneficial.

2.5.2 Absorbance measurement

Sample absorbance was measured at 400nm using disposable polystyrene cuvettes and a spectrophotometer (Camspec Ltd M100). Each sample was placed in a separate cuvette and blank absorbances with milli-RO purified water were first determined for each individual cuvette at each wavelength, to counter the effect of any variation between cuvettes (which were on the order of 15% - any greater than this were discarded). The spectrophotometer was regularly calibrated, and the zero point was checked after measurement of every sample at each wavelength. Cuvettes were replaced when their blank absorbance deviated more than 10% from the value when the cuvette was new.

2.5.3 Determination of DOC content

The method of Bartlett and Ross (1988) was used to determine actual DOC content in a subset of samples from each site throughout the study. Samples were also taken from streams elsewhere within the catchment of the River Tees (see Chapter 4) and these were also used in the calibration.

2ml aliquots of sample were used with 1ml each of H_2SO_4 and the manganese complex. Samples were transferred to clean cuvettes on which blank absorbance had first been determined, and absorbance was then determined at 495nm after 18 hours. Calibration standards were produced from dilution of a stock solution of oxalic acid made up to 100ppm C. Dilution was with milli-RO purified water.

2.6 Export budget calculation methods

In order to assess the changes in DOC export related to grip blocking, the results from the measurement programme described above were used to produce a detailed DOC budget for each of the monitored catchments, over the period of the study. The DOC budget was also calculated for the Trout Beck catchment from the data supplied by the ECN monitoring programme.

The derivation of a total budget from non-continuous measurements involves interpolation or extrapolation of concentration and flow measurements to produce a continuous export estimate, which can be integrated to estimate total export. A wide range of methods of varying complexity have been proposed for this (for example, Verhoff and Yaksich, 1982; Phillips et al, 1999; Olive and Rieger, 1988) and were summarised and compiled by (Phillips et al 1999). Although Phillips et al (1999) compiled the methods with reference to sediment loads, Littlewood (1995) suggests that these are generally applicable to mass load estimates, which would include DOC load. This will particularly be the case for those methods, including interpolation methods, that do not take account of differences between rising and falling hydrograph limbs or other hysteresis or exhaustion effects – such effects are likely to be process-based, and therefore less transferable between different systems such as sediment and DOC.

The application of each methodology involves error: the different natural behaviours emphasized by interpolation and extrapolation methods, inherent error in the method, and error due to varying sampling frequency. Load estimation methods assume a continuous (that is, short-interval) flow record and a non-continuous concentration record. In general, extrapolation methods first extrapolate the non-continuous concentration record into a continuous synthesised record based on some form of regression relationship or rating curve between flow and concentration. This synthesised record is then used to calculate flux for each interval of the high-frequency flow data.

Interpolation methods, by contrast, do not attempt specifically to rate or model the relationship between concentration and flow. Concentration at any particular point in the detailed flow record is estimated by interpolation of the nearest actual concentration measurements without necessarily attempting to explain the variation of the concentration between those points in terms of flow or any other causatory factor.

The commonly-used interpolation methods, as summarised by Phillips et al (1999) and Littlewood (1995) are:

$$Load = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\left(\sum_{i=1}^{n}\frac{Q_i}{n}\right)$$

Equation 2.2 "Method 1"

$$Load = K\sum_{i=1}^{n}\left(\frac{C_i Q_i}{n}\right)$$

Equation 2.3 "Method 2"

$$Load = K\sum_{i=1}^{n}\left(C_i \overline{Q}_p\right)$$

Equation 2.4 "Method 3"

$$Load = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\overline{Q_r}$$

Equation 2.5 "Method 4"

$$Load = K\frac{\sum_{i=1}^{n}C_i Q_i}{\sum_{i=1}^{n}Q_i}\overline{Q_r}$$

Equation 2.6 "Method 5"

where

C_i = instantaneous concentration (with "instantaneous" defined by the interval of the flow record);

Q_i = instantaneous flow;

n = number of samples in the record;

$\overline{Q}_p$ = the mean discharge between concentration samples;

$\overline{Q}_r$ = the mean discharge for the entire record period

K = conversion factor for the period of record, e.g. if Q is in L s^{-1} and the interval is 15 minutes, K = 15*60 = 900 to give the total load per interval

All these methods still require some instantaneous concentration value for each point of the flow record. Extrapolation and interpolation methods differ in how this instantaneous concentration estimate is developed from the non-continuous record. Extrapolation methods are less appropriate for species that have a strong seasonal component, such as DOC, as this will not be accounted for in the derived relationship between flow and concentration without the development of specific rating curves, which is beyond the scope of this study.

For the purposes of this study, method 2 (Equation 2.2) was adopted with instantaneous concentration values taken as being equal to the most recent actual concentration sample. This method is widely used, for example by the Department of the Environment to calculate fluvial pollutant loads to the North Sea (Littlewood, 1995).

2.6.1 Estimation of calculation errors

In any estimation of total export from non-continuous measurements of concentration and / or flow, there will be a degree of error caused by incorrect estimation of the change in either of these variables between measurements. The less frequent the sampling, the greater the probability of error as, for example, peaks in the hydrograph or concentration may fall between samples and be missed. Interpolation methods such as those given in Equation 2.2 – Equation 2.6 assume a flow record that is frequent enough to be assumed to be continuous, and concentration measurements which are less frequent. The approximation of the behaviour of the concentration record between samples will clearly involve a degree of error, as the change in concentration throughout events is not addressed directly.

These errors are often found by empirical studies to be surprisingly small, particularly in the case of dissolved loads – with sediments there is the possibility for huge peak loads, for example following a bank collapse during a flood, which can lead to far higher errors. One example of a study into the effects of decreasing sampling frequency is given by Johnson (1979). The study estimated phosphorus loads from a catchment with a flashy hydrograph, based on a total of 281 samples collected over a year. This sample set was then reduced in two ways. Firstly, by dividing the stream discharge into quartiles and taking the same size subset of samples from each quartile. Secondly, by taking a subset of samples without reference to hydrograph – this second method is comparable to the present study where samples were taken at fixed intervals without reference to flow. In both cases, even weekly samples were found to provide a satisfactory estimate of the load compared to the full dataset (Johnson, 1979). Another example is given by Robertson and Roerish (1999): that study compared budgets calculated from daily flow and concentration records to those calculated from various sub-sampling strategies. It was found that semi-monthly fixed-interval sampling provided the best estimate relative to the daily series, and that augmenting the fixed-interval sampling with flow proportional sampling in an attempt to ensure that storm peaks were captured actually decreased the accuracy of the estimate over longer (>1 year) record periods (Robertson and Roerish, 1999).

The data collected in this study for the four grip sites and the stream at Widdybank consisted of a flow record that was collected originally at a 15-minute frequency, and DOC concentration measurements at a frequency of 8 hours for the majority of the record period. However, the modelled reconstruction of the flow series for each site was produced on a 6 hour timestep, whilst for Trout Beck although flow records were available on a 15 minute timestep, DOC concentration samples were only available on a weekly timestep.

Two separate assessments of the error in the budget calculations are therefore required for these budgets. Firstly, to estimate the error that is involved in calculation of export budgets by interpolation methods, based on the 15 minute timestep flow record and 8 hour timestep DOC record. Secondly, to estimate the extent to which this error increases with both decreasing sample frequency (for Trout Beck) and decreasing flow record frequency (for the modelled flow records at the grip sites).

Littlewood (1995) showed that the inherent error in the budget calculation methods cannot be calculated rigorously due to the large number of unknown factors including both the response time of the flow and concentration, and the relationship that in reality may exist between the two variables but which is ignored by interpolation methods. However, Harrison et al (1990) provided a method for estimating the inherent error in the budget calculation methods. Applied to the 15 minute flow and 8 hour sampling records, this gives an estimate for the error in the load calculated by Method 2 of 8.9% (F. Worrall, pers. comm). This error is inherent in the budget calculation method and is not due to measurement error: it must therefore be considered to be consistent between the monitored sites.

In order to assess the likely error in the Trout Beck estimates introduced in the change from sub-daily sampling to weekly sampling, 100 sets of 52 data points were selected at random from the full-resolution Widdybank dataset. This gave 100 estimates of the yearly flux for Widdybank calculated from a "weekly" dataset, against which the flux calculated on the basis of the full sub-daily sampling dataset can be compared. This approach is similar to that of the SMILER algorithm described by Littlewood (1995). The mean difference in the budget estimations from the two sampling frequencies was 3.3%.

Therefore, taking the 8-hour sampling frequency as a "continuous" record, the estimated error for the grip sites and Widdybank sites is 8.9% where budgets are calculated from the 15-minute flow record. For Trout Beck the estimated error is (8.9 + 3.3) = 12.2%.

Furthermore, as discussed in section 2.4.3.2 the final flow record produced by modelling for each site was a 6-hourly record rather than the 15-minute raw data. For consistency between sites, where observed rather than modelled data was used this was also aggregated to a 6-hour record. To estimate the errors caused by this aggregation of the flow in comparison to the 15-minute flow record that was originally envisaged for all sites, budgets were also calculated following the same method for the Hexham 2 and Widdybank sites (where 15-minute flow data was available) from the original 15-minute continuous flow record, in addition to the 6-hour aggregated record, with identical values for the concentration record in each case.

In order to match up the 6-hour flow record with the irregular (but always coarser than 6-hour) concentration record, both datasets were converted to a common divisor timestep, chosen as 15 minutes for ease of comparison with the original logged data. For the 6-hour modelled flow record, this was achieved as for the concentration data, by taking flow at each timestep to be equal to the most recent 6-hour flow value. This will introduce further error, in addition to that introduced by the interpolation of the concentration record, as the flow is assumed to remain constant for 6 hours, then change as a step function for the next 6 hours. The same process was followed to convert the observed 15-minute flow record, where available, to a 6 hour record. Taking the mean value for each 6 hour period, rather than the first sample in the period as was done, would arguably be a more accurate method but this would not be consistent with the structure of the modelled flow record.

Results from budgets calculated both from the 6-hour data (modelled or observed) are presented along with those calculated from the 15-minute flow record in section 2.7 The difference between the two budget calculations was generally low, only exceeding 10% at Hexham 2 in one month (Table 2.13). With reference to the above discussion on error estimation techniques, it should also be noted that the majority of the work in this study is focused on comparing the differences between the blocked and unblocked sites. Since the same change from 15-minute to 6-hour data was applied to all sites except Trout Beck, the impact of the difference in timesteps in terms of the comparison between those sites will be reduced.

2.7 Results

2.7.1 Flow modelling

IHACRES flow models were developed from different periods of observed data for each catchment, dependent on the availability of good flow data. Calibrations were selected to cover periods with as wide a variety as possible of flow and temperature conditions to ensure a robust model. Due to the extremely flashy nature of the hydrograph from all catchments, calibrating only over a storm event or only over a low flow period would result in an extremely inaccurate model.

The quality of fit of the IHACRES flow models were assessed during model development based on the R^2 value of the regression between observed and modelled flow for the calibration period, and also on the overall model bias (the annual error in runoff, in mm). The modelled and observed hydrographs were also compared visually, especially to ensure that fit was satisfactory during both high and low flow periods. Results are presented in the order models were developed, starting with Hexham 2 which had the best flow record of the drained catchments.

2.7.1.1 Hexham 2

The Hexham 2 model was developed and tested first, as this site had the most complete flow record, and therefore the best range of calibration periods. The model was calibrated over the period 21st February 2004 – 2nd December 2004, this being the longest continuous period in the record with no missing data in the flow, rainfall, or temperature records. For this period, the model was calibrated with the following settings for each parameter in the non-linear loss module:

T_w	15
f	1.5
T_{ref}	20
I	0
p	1

Table 2.1 Hexham 2 IHACRES parameters

With this calibration the model predicted flow during the calibration period with $R^2 = 0.789$ and Bias (overall error in flow volume) of 21.84 mm yr^{-1}. The highest efficiency model that could be found was $R^2 = 0.800$, which was achieved for several calibrations by setting lower values for both T_w and T_{ref} than those above. However in all these cases the bias was much higher, ranging from 174.76 mm yr^{-1} to 206.74 mm yr^{-1}. The model calibration given above was therefore accepted and used to simulate flow for periods of no flow record. The modelled and observed hydrographs for the calibration period are shown in Figure 2.6(b).

2.7.1.2 Hexham 3

Two models were produced for the Hexham 3 site, based on the flow record produced by the Druck / Campbell logging system, and that produced by the Intelisys system. For the Campbell data the longest continuous period in the flow record which contained no data gaps and which represented a suitable range of flow conditions, as opposed to only dry periods of no flow, was the period 26th September – 3rd December 2003. This period was preceded by a drought period of little or no flow in the catchments, but itself contained a wide range of events. For this period, the following settings were chosen for the non-linear loss module parameters:

T_w	30
f	5
T_{ref}	10
I	0
p	1

Table 2.2 Hexham 3 Campbell IHACRES parameters

Compared with the Hexham 2 model, the drying rate at the reference temperature is higher. This is as expected for a smaller catchment which would have a flashier hydrograph response. The temperature dependence of the drying rate is also higher. This could be explained by the fact that the drain channel in this catchment is somewhat shallower than the Hexham 2 drain, and therefore will drain water only from the shallower peat layers which are more exposed to temperature fluctuations. This calibration produced a model efficiency during the calibration period of $R^2 = 0.841$ and bias = 50.67 mm yr^{-1}.

For the Intelisys data, the calibration period chosen was 28th March 2004 – 28th October 2004, being the period from the installation of the Intelisys equipment to the first equipment failure. This period included a wide range of flow conditions from periods when the grip was observed to be dry, to extreme storm events in August and October. It was found that models developed for this data had low efficiencies, although visually the fit to between the observed and modelled hydrographs was good. It was not possible to entirely filter out temperature effects from the poorly-compensated Intelisys sensor data and therefore the observed flow record contains a daily temperature-derived fluctuation. This causes scatter in the relationship between modelled and logged values, and therefore the R^2 value for the model is low. Furthermore, all the models produced from this data tended to systematically overpredict flow. The best model that could be achieved for this data was with the following parameters:

T_w	30
f	4
T_{ref}	20
l	0
p	1

Table 2.3 Hexham 3 Intelisys IHACRES parameters

This resulted in an R^2 for the calibration period of 0.583 and bias of 488.26 mm yr^{-1}. Despite these results the output from the Campbell and Intelisys models over the whole record period correlated well, with $R^2 = 0.947$. Therefore the output of the Campbell model was selected to simulate flow for the periods of no flow record, despite the short calibration period. The modelled and observed hydrographs for the calibration period are shown in Figure 2.6(c).

2.7.1.3 Hexham 1

For the Hexham 1 site, models were also produced based on both the Campbell and the Intelisys system data. The calibration period for the Campbell data was 24th September 2003 – 6th December 2003.

T_w	35
f	3
T_{ref}	15
l	0
p	1

Table 2.4 Hexham 1 Campbell IHACRES parameters

Model fit for the calibration period was R^2 = 0.839 and Bias = -1.569 mm yr^{-1}.

Modelling the Intelisys data for this site produced similar behaviour to modelling the Hexham 3 Intelisys data.

T_w	20
f	3
T_{ref}	20
l	0
p	1

Table 2.5 Hexham 1 Intelisys IHACRES parameters

The fit of the resultant model was low owing to uncorrected temperature effects in the data, with R^2 = 0.597 and bias = 30.243 mm yr^{-1}. However the correlation between the output from the Campbell and Sentry models was good, R^2 = 0.860, and so once again the output from the Campbell model was selected to simulate flow for the periods of no flow record. The modelled and observed hydrographs for the calibration period are shown in Figure 2.6(a).

2.7.1.4 Cowgreen

Due to animal interference, weather damage and consequent restricted site access, and other equipment failures, the recorded flow record for this site had many breaks and relatively few uninterrupted periods of good data as required for calibration. Even a single missing data point must be filled in, for the IHACRES model to be calibrated. Reconstruction of the flow record for this site presented a further challenge, as in addition to temperature-related damage to transducers causing gaps in the flow record, the site also suffered from gaps in the rainfall record caused by animal damage to the rain gauge installation and to datalogger connections, unlike at the Hexhamshire sites where an uninterrupted rainfall record was available.

Transducer failure is identified in the logged record from the negative apparent pressures recorded by the datalogger and a subsequent warning value being recorded by the datalogger program. However, rain gauge failure is often silent and it is not always possible to tell from the record when the instrument failed, as either a failed rain gauge or the genuine absence of rain will both result in no rain being recorded. Equally, at times rainfall values were recorded when the rain gauge was known to be broken; this was due to short circuits in a damaged cable causing the datalogger to register a pulse that was recognised as a rain gauge signal.

The ECN monitoring site at Moor House located at NY758335, approximately 4.5km from the Cowgreen site, operates a rain gauge installation (ECN 2006b) from which hourly data was obtained for the period of the project. Regular monitoring of this site, in addition to animal-proof fencing, ensures that this data record has few gaps, and that those gaps which do exist are well documented.

The Moor House rainfall dataset was used firstly to identify periods in the Cowgreen record where the rainfall series was potentially inaccurate or missing. Secondly, for these periods the Moor House record was used in place of the Cowgreen record, as the correlation between the records at other times was found to be good.

Analysis of the Moor House data record for the period September 2002 – June 2005 revealed only 7 periods of over 7 days with no recorded rainfall (Table 2.6) whilst the Cowgreen data showed more significant gaps (Table 2.7).

Dates	*Length of rain-free period*
13/02/2003 - 22/02/2003	8.5 days
03/04/2003 - 13/04/2003	10.5 days
29/08/2003 - 06/09/2003	7.75 days
27/12/2003 - 04/01/2004	8.5 days
24/02/2004 - 04/03/2004	8.75 days
04/06/2004 - 29/07/2004	55.5 days (known equipment failure)
18/02/2005 - 27/02/2005	9 days

Table 2.6 Dry periods over 7 days in the Moor House rainfall record

Dates	*Length of rain-free period*
19/03/2003 - 31/03/2003	12.75 days
01/04/2003 - 14/04/2003	12.5 days
24/05/2003 - 04/06/2003	11 days
08/07/2003 - 17/07/2003	8.75 days
01/08/2003 - 10/08/2003	8.75 days
14/08/2003 - 04/09/2003	20.75 days
04/11/2003 - 26/12/2003	52.5 days
29/12/2003 - 27/05/2004	149.5 days
14/08/2004 - 25/08/2004	10.75 days
25/09/2004 - 07/10/2004	13 days
12/01/2005 - 30/06/2005	169.25 days (equipment removed)

Table 2.7 Dry periods over 7 days in the Cowgreen rainfall record

During the periods where rainfall data was good for both sites the correlation between rainfall at the two sites was good, in terms of the total rainfall over the period under comparison, and also the number of days on which rain occurred. The rainfall record for the Cowgreen site was therefore reconstructed as follows:

- Substituting Moor House rainfall values where the Cowgreen rainfall gap was greater than 7 days
- Using the Cowgreen rainfall values in all other places except
  - 20^{th} – 31^{st} October 2003
  - August 2004
  - October 2004
- During these times, the Cowgreen raingauge is known to have been non-operational or not installed, but some spurious data points were generated by short circuits or other wiring faults, meaning that gaps of over 7 days are not observed in the rainfall record.

The IHACRES model was calibrated and run using the rainfall series as described, over the calibration period 29^{th} May – 11^{th} July 2004. It is acknowledged that the calibration period for this site was short; this was the longest period without any missing data points. However the calibration was also repeated for another period of similar length (6^{th} April – 19^{th} June 2003) and the resultant flow simulations were similar; the 2004 calibration was used as it included a wider range of storm events. The resultant IHACRES model parameters were as shown in Table 2.8. R^2 for the calibration period was 0.57 and Bias = -57 mm yr^{-1}. The modelled and observed hydrographs for the calibration period are shown in Figure 2.6(d). The somewhat lower quality of the model for this site can be observed in the hydrographs with the model in particular predicting small flow events following slight rainfall in generally dry periods that are not observed in the recorded hydrograph. However, the model inaccuracies are biased towards small transient "events" in dry periods, which form only a small proportion of the overall export.

T_w	30
f	1.5
T_{ref}	15
l	0
p	1

Table 2.8 Cowgreen (Campbell) IHACRES model parameters

2.7.1.5 Widdybank Fell

The flow record for this site suffered from few gaps. The higher flow and greater depth of the stream compared to the grip sites meant that the stream froze less often, and never to an extent that the transducer was damaged. The physical situation of the site and its location within the Moor House NNR also meant that it was less prone to damage by animals, and cables could be more completely buried to further minimise this risk.

The only gaps in the recorded flow record occurred from 11/08/2004 – 16/08/2004 and 30/08/2004 – 22/09/2004, where the datalogger itself was damaged by flooding after extreme storm events. The following IHACRES model parameters were used to reconstruct the flow record for these periods:

T_w	15
f	2
T_{ref}	15
l	0
p	1

Table 2.9 Widdybank IHACRES model parameters

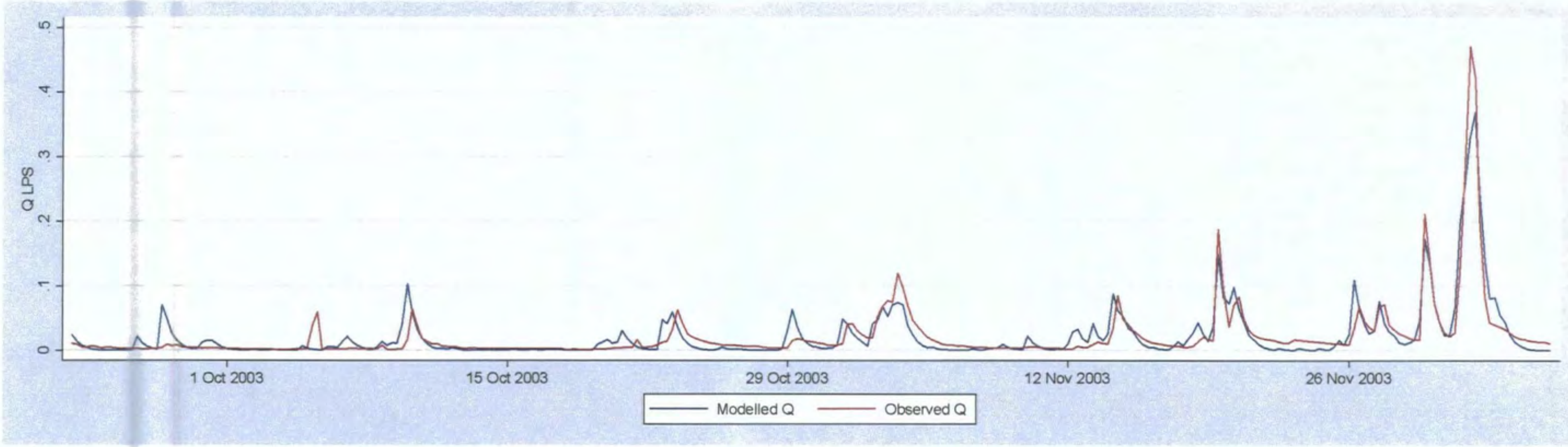
However, for this site a significant baseflow contribution is observed in the field. This was confirmed in the flow modelling, where a better model was achieved by calibrating the linear module as a "2 exponential stores in parallel" structure, i.e. a baseflow store and a quickflow store, both with access to the stream. Model efficiency with these parameters was R^2 = 0.820 and bias = 24.166 mm yr^{-1}. Output from this model was used to fill in the flow record during the periods detailed above. The modelled and observed hydrographs for the calibration period are shown in Figure 2.6(e).

There was no raingauge at the Widdybank Fell site and the rainfall record used was that from the Cowgreen site, itself partially reconstructed from the Moorhouse rainfall record as detailed in section 2.7.1.4.

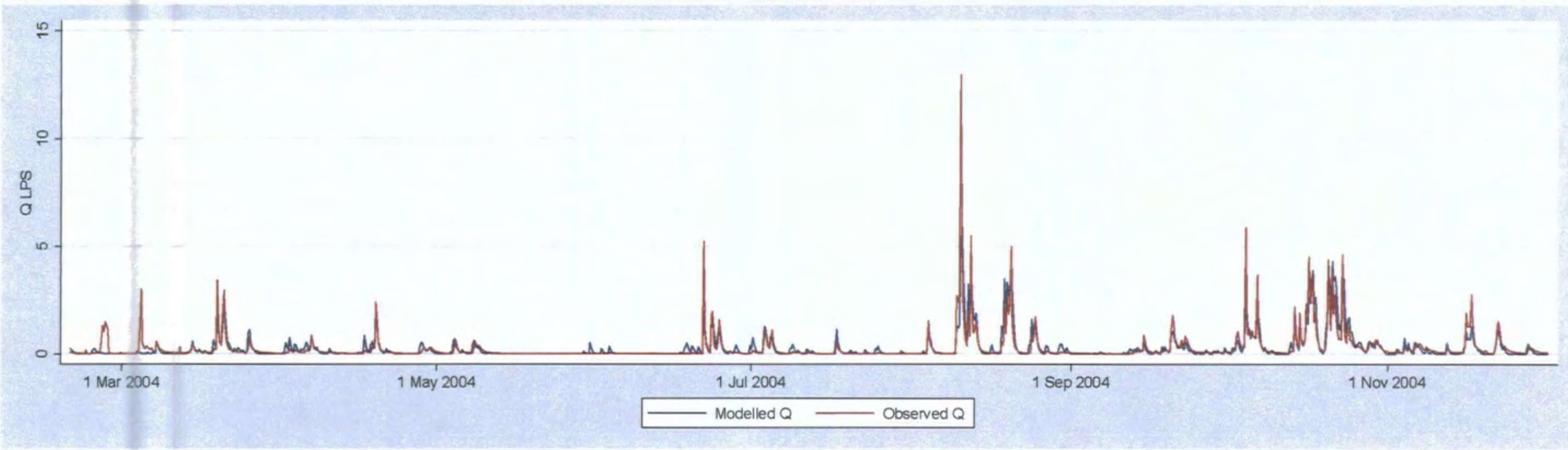
2.7.2 Hydrograph choice

The rainfall records for the Hexhamshire Common and Teesdale sites are shown in Figure 2.7(a) and Figure 2.8(a), along with the final hydrographs resulting from the observed data and the IHACRES modelling. Due to the many irregular gaps in the flow record from Hexham 1, Hexham 3, and Cowgreen, the final hydrograph from these sites consisted entirely of the IHACRES model output based on the Campbell input data. For Hexham 2 the hydrograph was partially modelled and partially observed, as indicated by the shading in Table 2.11, while at Widdybank the hydrograph was observed at all times with the exception of August – September 2004 where the modelled data were used. For Trout Beck, the discharge dataset was that provided by the ECN, aggregated to a 6-hour timestep for consistency with the other sites.

a)

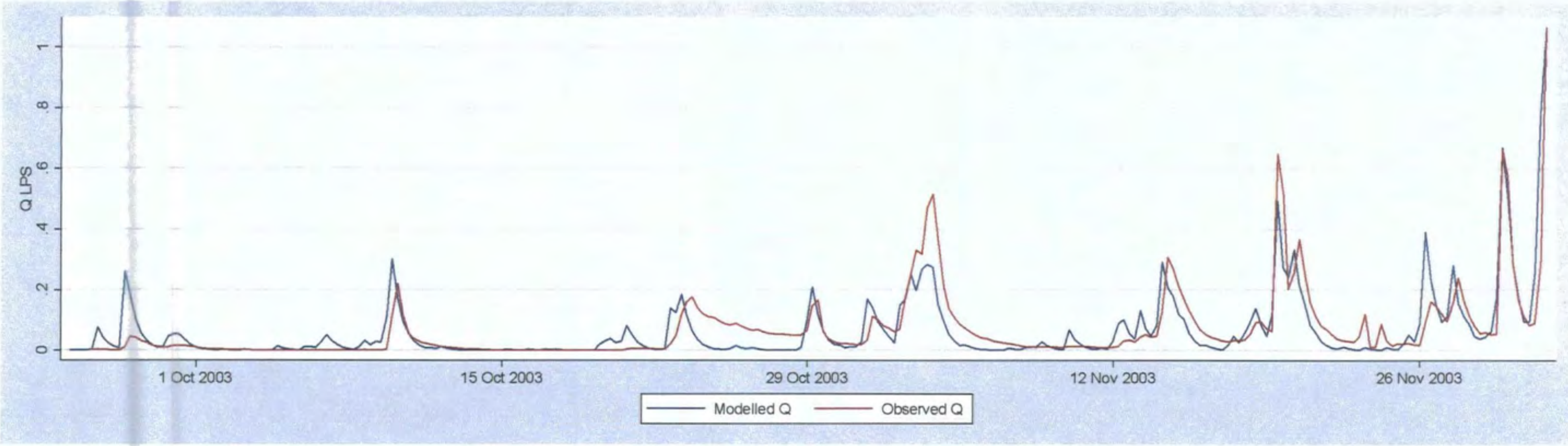


b)

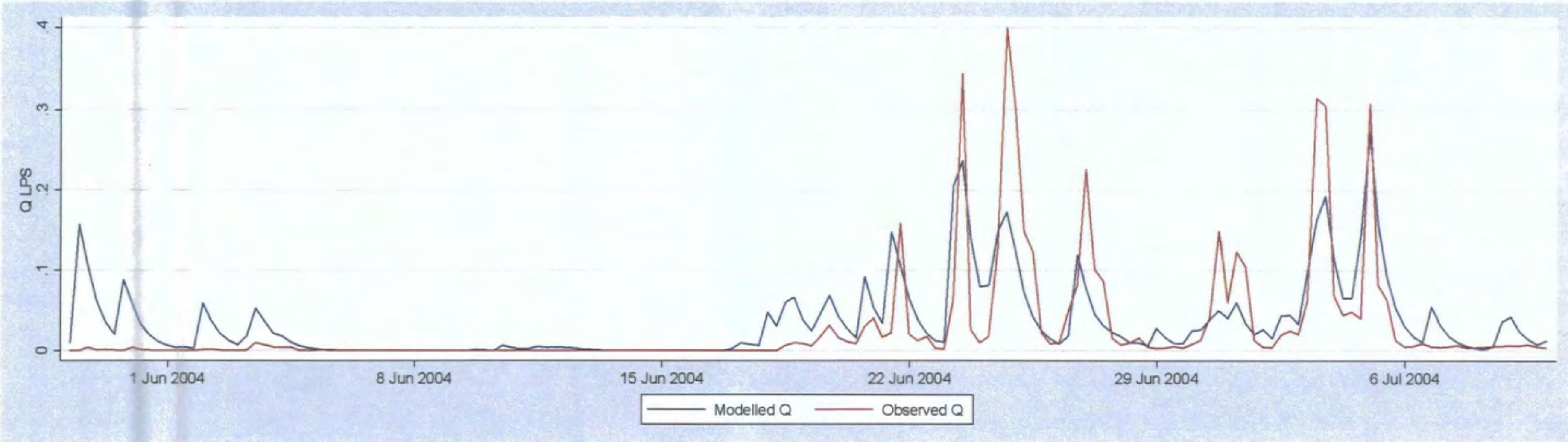


Legend on p.62

c)



d)



Legend on p.62

e)

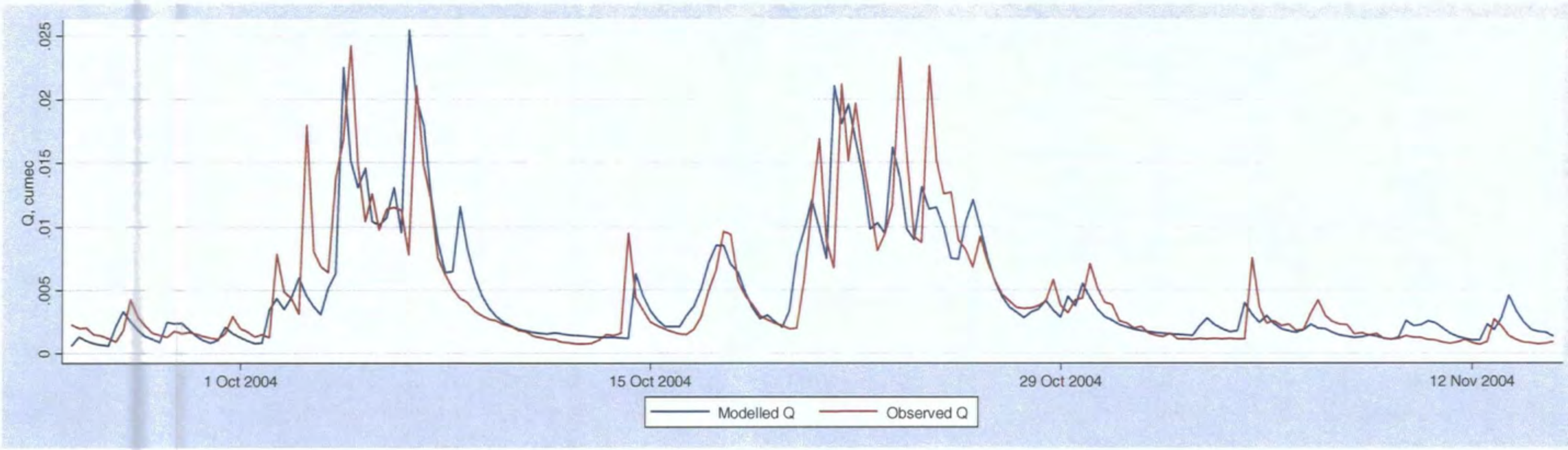
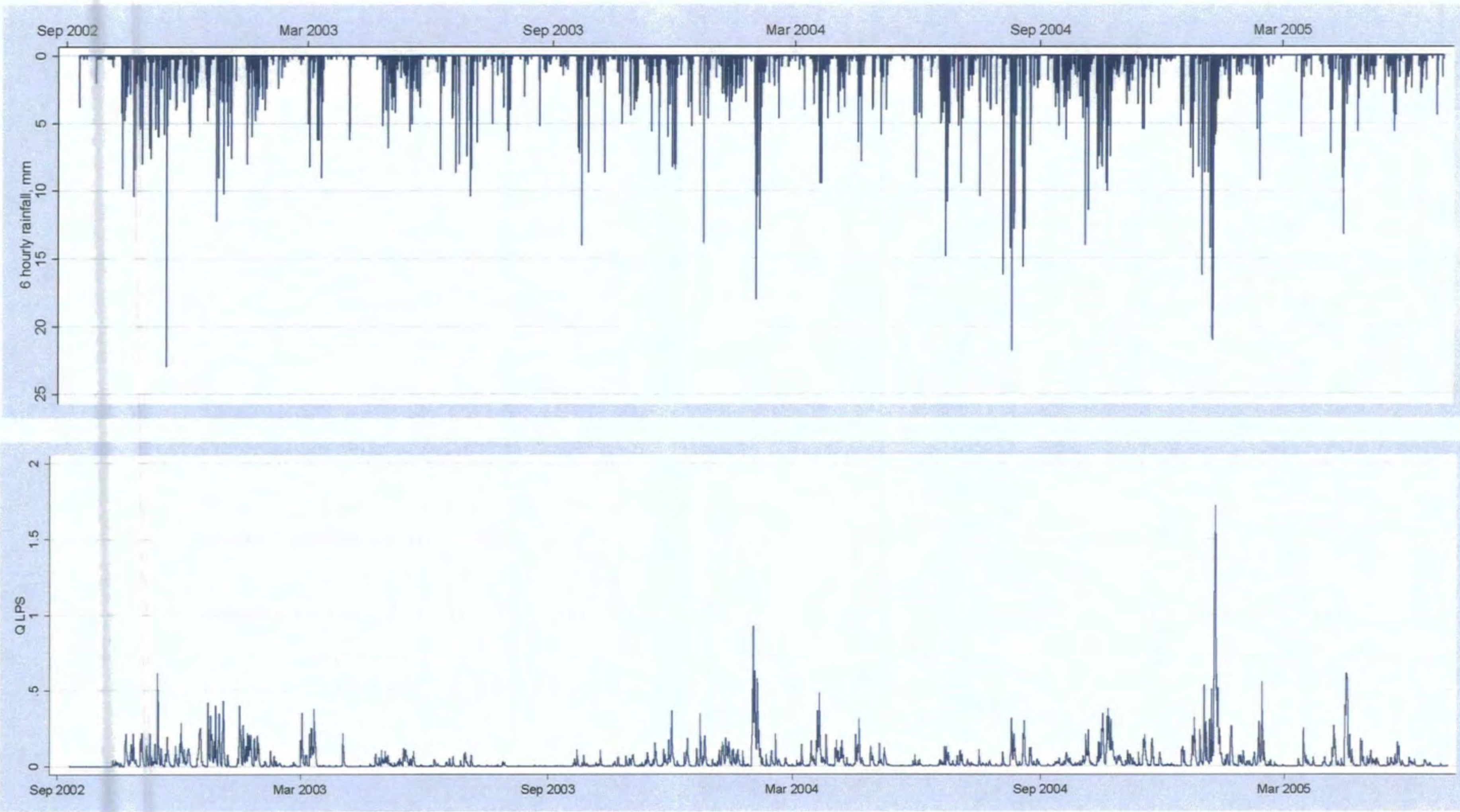


Figure 2.6 Modelled and observed hydrographs for the model calibration periods

a) Hexham 1 b) Hexham 2 c) Hexham 3 d) Cowgreen e) Widdybank

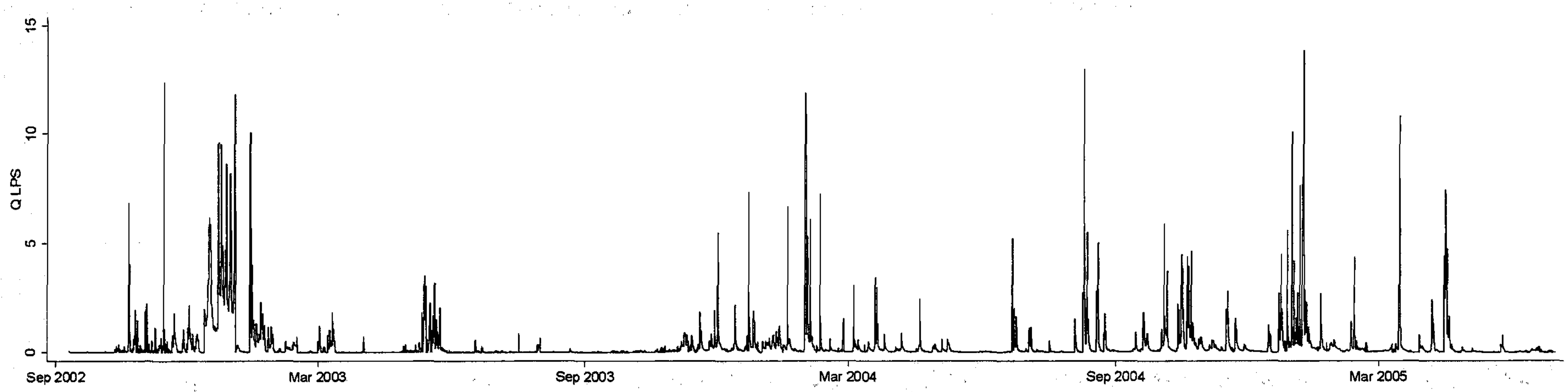
a)

b)



Legend on p.64

c)



d)

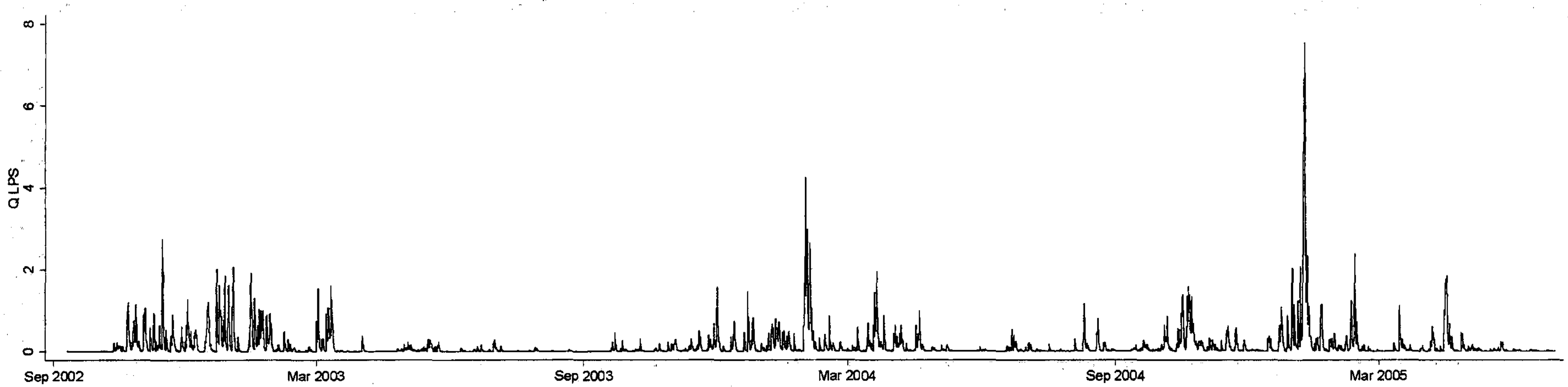
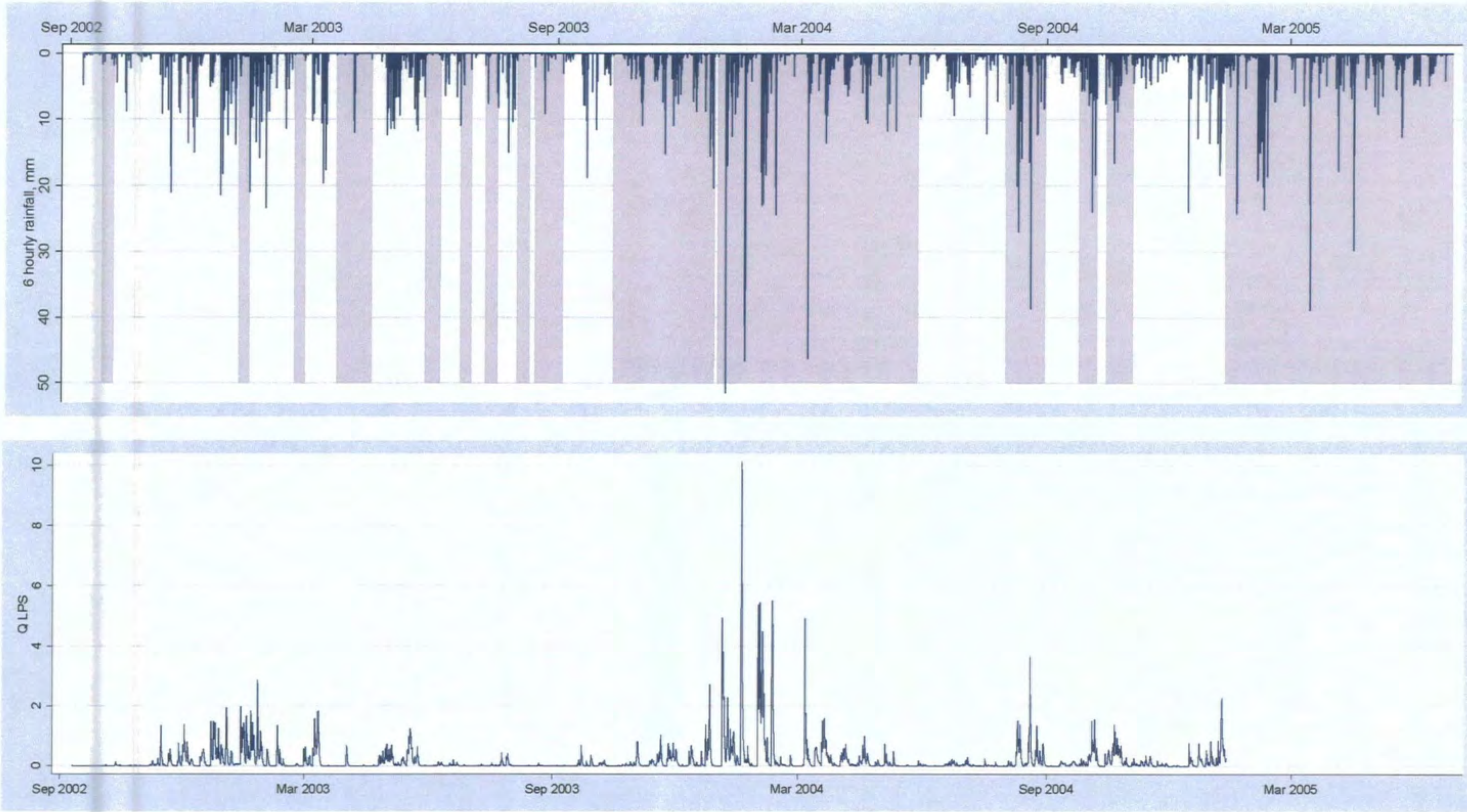


Figure 2.7 Hexhamshire common rainfall and combined observed / modelled hydrographs for the study period

a) 6 hourly rainfall b) Hexham 1 hydrograph c) Hexham 2 hydrograph d) Hexham 3 hydrograph

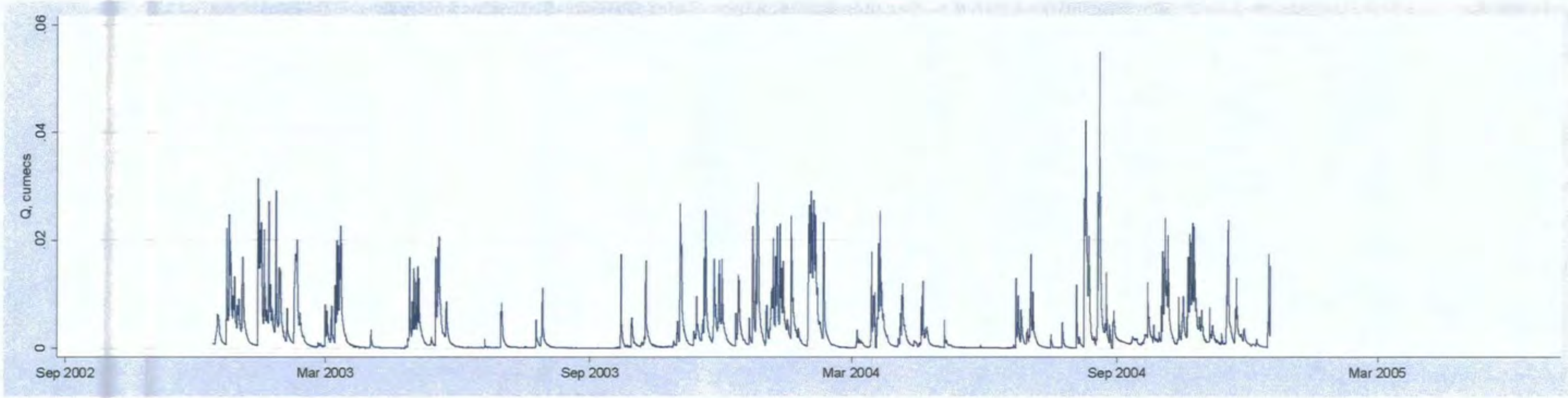
a)

b)



Legend on p.66

c)



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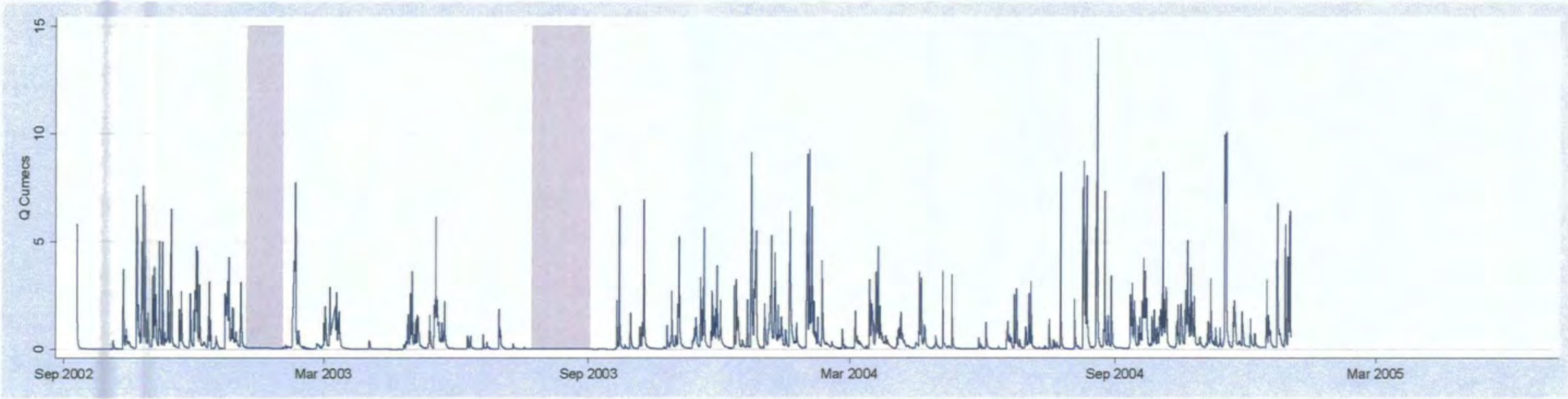


Figure 2.8 Teesdale rainfall and combined observed / modelled hydrographs for the study period

a) Teesdale 6-hourly rainfall for the study period. Shaded portions of the chart indicate where rainfall record is reconstructed from the Moorhouse data.

b) Cowgreen hydrograph c) Widdybank hydrograph d) Moorhouse hydrograph (shaded portions indicate missing data)

2.7.3 DOC calibration

DOC calibration experiments were conducted on samples taken from all five study catchments, in addition to other upland streams studied in Chapter 4. Analysis was performed throughout the study period on samples covering a wide range of flow conditions. A consistent linear fit was found between DOC content as determined though this method, and sample absorbance at 400nm (Figure 2.9). No significant differences ($P < 0.05$) were observed between the different sites in the calibration coefficients of the absorbance vs. DOC relationship.

However, it should be noted that this is not always the case; in particular recent work by Wallage et al (in review) does suggest that a stable relationship may not be a robust assumption and that in some circumstances the relationship between colour and DOC content may exhibit variation with time since blocking of a drain. In these data, the gradient of the relationship between absorbance at 400nm and DOC content was not found to differ significantly between sites ($P < 0.05$), so a single calibration relationship was adopted as indicated by the best-fit line in Figure 2.9 and by Equation 2.7. There is considerable scatter in the relationships for all grip sites which may obscure any differences in the relationships based on time since blocking in line with those observed by Wallage et al (in review); but nevertheless such a hypothesis is not implicitly supported by these data and a single calibration relationship is adopted.

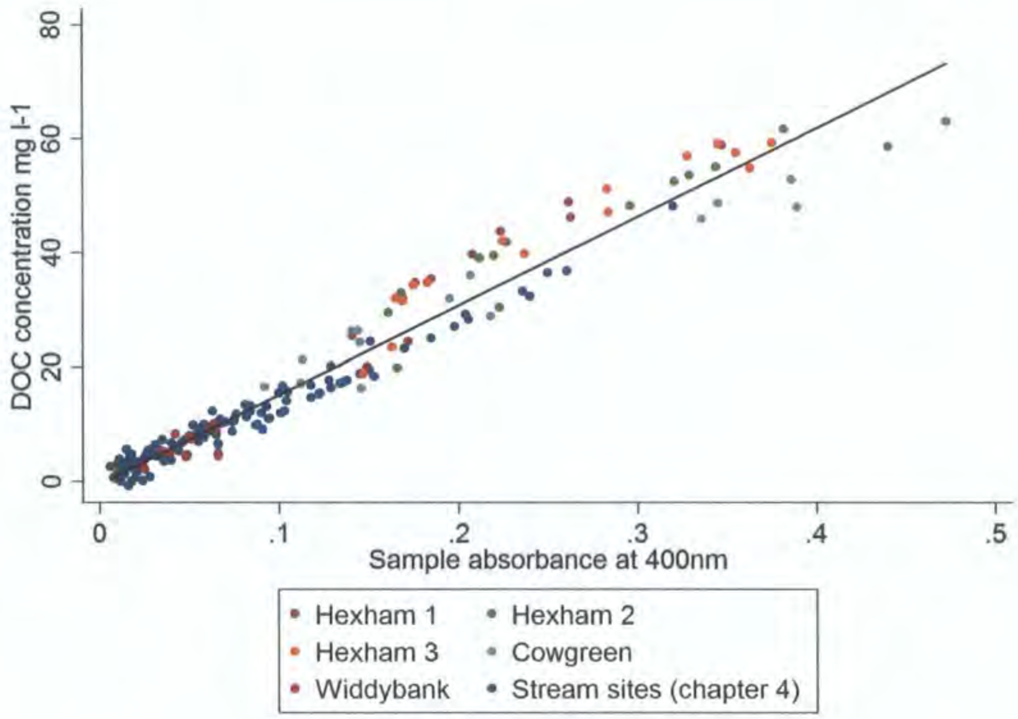


Figure 2.9 Calibration for sample absorbance vs. DOC content

Best fit line shown for all samples taken together representing Equation 2.7. Gradient of calibration was not significantly different between sites (P<0.05)

$$DOC(mg/L) = 156.08Abs_{400} - 0.4347 \text{ (R}^2 = 0.956\text{, n=205)}$$

Equation 2.7 Calibration equation for sample absorbance vs. DOC content

The calibration obtained was used to calculate DOC content for all samples from the corrected 400nm absorbance measurements. This calibration equation implies a minimum detection threshold for DOC when $Abs_{400} \leq 0.0028$ (that is, 0.4347/156.08), below which a DOC concentration of 0 mg l^{-1} was recorded. However, this is on the limit of accuracy of the spectrophotometer, and in any case values this low were only ever recorded in a small number of samples from the Widdybank catchment and some non-peat stream catchments.

2.7.4 DOC Sampling

The DOC sampling record was largely consistent between sites, with similar total numbers of samples from each catchment (Table 2.10). A total of 5800 samples were collected and analysed for absorbance during the study period. The slightly lower number of samples obtained from the Hexham 1 catchment is due to this grip, being the smallest catchment studied, drying up more frequently in summer and also being more prone to freezing in winter. The Hexham 2 and Widdybank catchments were not instrumented with samplers until the beginning of January 2003. Samples were collected manually from Trout Beck on a weekly basis.

Month	*Hexham 1*	*Hexham 2*	*Hexham 3*	*Cowgreen*	*Widdybank*
Nov-02	51	0	51	51	0
Dec-02	54	0	65	55	0
Jan-03	48	26	47	30	26
Feb-03	6	23	4	9	25
Mar-03	16	83	49	57	39
Apr-03	36	44	52	42	48
May-03	56	57	57	42	55
Jun-03	17	21	25	25	25
Jul-03	15	31	27	30	31
Aug-03	5	16	18	43	48
Sep-03	32	32	32	61	23
Oct-03	88	77	63	85	38
Nov-03	82	81	81	81	75
Dec-03	53	36	49	44	50
Jan-04	50	51	51	48	57
Feb-04	41	47	48	29	31
Mar-04	50	65	63	23	23
Apr-04	41	75	76	41	55
May-04	25	57	75	61	75
Jun-04	0	30	26	19	29
Jul-04	30	30	28	30	31
Aug-04	17	24	18	24	32
Sep-04	34	61	61	61	62
Oct-04	93	93	93	93	93
Nov-04	70	78	78	79	78
Dec-04	26	26	33	29	34
Jan-05	16	16	16	0	0
Total	**1052**	**1180**	**1286**	**1194**	**1088**

Table 2.10 Number of samples collected and analysed for DOC content from each catchment in each month of the sampling campaign

2.8 DOC Budget Calculations

From the results given in section 2.7, dissolved organic carbon budgets were calculated according to Method 2 and are presented in Table 2.11. In summary, for each of the five main sites these budgets are calculated from the following data:

- Flow records that were derived from a combination of observed and modelled data, as indicated. For the Hexham 1, Hexham 3, and Cowgreen sites, budgets for every month are calculated from the modelled flow series as periods of good observed data were shorter and more broken up at each of these sites. For the Hexham 2 and Widdybank sites the budgets are calculated from observed data where available and modelled data at other points. The hydrograph records used in each budget calculation are shown in Figure 2.7 and Figure 2.8. Hydrographs are on a 6 hour timestep. Modelled data is produced on a 6-hour timestep, and observed data is aggregated from 15-minute observations to 6-hour data. The exception is the Hexham 2 and Widdybank 15-minute budgets included for comparison in Table 2.13, which are calculated from the 15-minute observed flow series.

- DOC concentration that was calculated from absorbance measurements at 400nm and the DOC vs. absorbance calibration relationship described in section 2.7.3 and Figure 2.9.

- Net catchment exports are calculated by integration following Method 2 (Equation 2.3). Instantaneous loads are calculated for each 15 minute timestep based on the flow value taken to apply to that timestep and the most recent DOC measurement, and loads are summarised for each month and year.

- Areal exports are calculated from catchment areas and net catchment exports, as described in section 2.2 and section 2.6 respectively.

- The Trout Beck budgets are calculated using Method 2 from the discharge and weekly DOC data supplied by the ECN from their monitoring programme.

Budgets are calculated separately for each calendar month over the record period and are expressed in terms of tC km^{-2} $month^{-1}$. Budgets are given in Table 2.11 and the table is colour coded to represent the flow series that was used to derive the budget for each month (key in Table 2.12). The monthly budget time series are also represented graphically in Figure 2.10.

Month	Hexham 1	Hexham 2	Hexham 3	Cowgreen	Widdybank Fell	Trout Beck
Nov-02	3.832		5.825	3.646		
Dec-02	4.322		12.281	6.333		
Jan-03	3.921	1.680	10.458	10.159	1.872	0.522
Feb-03	0.371	0.366	1.052	1.926	2.008	0.634
Mar-03	1.942	1.602	5.183	2.341	2.292	0.524
Apr-03	0.762	0.851	0.822	5.295	0.762	0.207
May-03	1.798	6.556	2.699	8.590	4.839	1.365
Jun-03	0.508	1.838	0.858	3.053	0.061	0.127
Jul-03	0.692	2.991	1.741	3.061	1.625	0.801
Aug-03	0.032	0.422	0.302	0.500	0.144	0.799
Sep-03	0.843	1.376	1.651	1.144	0.507	0.322
Oct-03	0.487	0.337	1.330	0.560	1.315	0.932
Nov-03	1.835	2.976	4.765	3.892	8.586	2.789
Dec-03	2.804	6.429	7.501	3.389	5.456	1.419
Jan-04	4.206	10.911	10.612	11.995	6.687	1.846
Feb-04	5.079	7.798	12.072	15.555	3.043	1.013
Mar-04	2.979	3.733	7.557	2.877	0.496	1.016
Apr-04	3.776	2.629	7.140	4.387	3.043	0.674
May-04	2.377	1.353	1.078	2.936	0.404	0.331
Jun-04		3.387	2.580	2.360	1.597	0.946
Jul-04	1.677	2.436	1.733	2.191	2.744	1.210
Aug-04	4.004	18.744	6.246	25.192	17.016	6.862
Sep-04	1.327	4.379	2.008	3.011	2.260	1.583
Oct-04	4.634	13.554	11.169	11.879	10.214	2.603
Nov-04	2.374	6.107	4.827	3.647	4.862	2.087
Dec-04	2.814	9.928	5.217	3.749	0.790	1.339
Jan-05	8.590	10.799	15.770			
2003 Total	**15.995**	**27.424**	**38.362**	**43.910**	**29.467**	**10.441**
2004 Total	**35.247**	**84.959**	**72.239**	**89.779**	**53.156**	**21.509**

Table 2.11 Monthly DOC export budgets for each catchment. All units are in tC km^{-2} $month^{-1}$ or tC km^{-2} $year^{-1}$

Key in table	Flow record type used for month
	Observed 6-hourly data only
	Modelled 6-hourly data only (used where >20% of observed data is missing)
	Partially modelled, partially observed data (>1 day/month modelled)
	ECN data
	No DOC samples taken in month so no budget calculated

Table 2.12 Colour key for Table 2.11, indicating source of hydrograph used in DOC export budget calculations

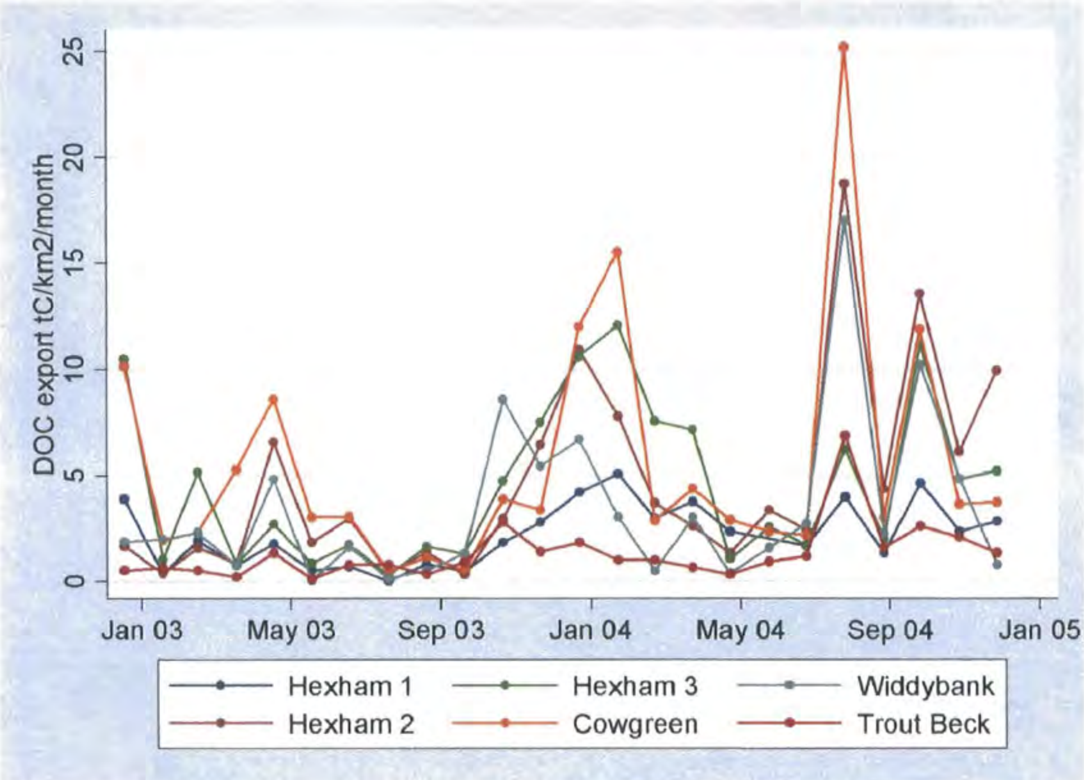


Figure 2.10 Monthly export budgets for each catchment, as presented in Table 2.11

Budgets were also calculated for the Widdybank and Hexham 2 catchments from the observed 15-minute data, where this was available, and the percentage difference between the budget estimates according to the 6 hour observed data and the 15 minute data was calculated for each month (Table 2.13). It was found that the two estimates agreed well, and therefore the 6-hour aggregated flow record was considered suitable for budget calculations.

Month	*Widdybank 15 minute budget*	*Widdybank 6hr budget*	***% diff***	*Hexham 2 15 minute budget*	*Hexham 2 6hr budget*	***% diff***
Jan-03	1.872	1.872	**0.00**			
Feb-03	2.002	2.008	**0.30**			
Mar-03	2.291	2.292	**0.03**			
Apr-03	0.755	0.762	**0.84**			
May-03	4.839	4.839	**0.01**			
Jun-03	0.067	0.061	**-8.13**			
Jul-03	1.613	1.625	**0.79**			
Aug-03	0.139	0.144	**3.61**			
Sep-03	0.480	0.507	**5.61**			
Oct-03	1.330	1.315	**-1.13**			
Nov-03	8.779	8.586	**-2.20**			
Dec-03	5.398	5.456	**1.08**			
Jan-04	6.575	6.687	**1.71**	10.914	10.911	**-0.03**
Feb-04	2.956	3.043	**2.93**	7.110	7.798	**9.68**
Mar-04	0.490	0.496	**1.36**	3.626	3.733	**2.95**
Apr-04	3.074	3.043	**-1.02**	2.654	2.629	**-0.95**
May-04	0.410	0.404	**-1.55**	1.351	1.353	**0.16**
Jun-04	1.583	1.597	**0.88**	3.081	3.387	**9.94**
Jul-04	2.696	2.744	**1.77**	2.390	2.436	**1.92**
Aug-04	16.472	17.016	**3.30**	20.942	18.744	**-10.50**
Sep-04	2.226	2.260	**1.54**	4.434	4.379	**-1.25**
Oct-04	10.536	10.214	**-3.06**	14.484	13.554	**-6.42**
Nov-04	4.867	4.862	**-0.11**	6.112	6.107	**-0.08**
Dec-04	0.872	0.790	**-9.43**			
2003 Total	29.565	29.467	**-0.33**			
2004 Total	52.757	53.156	**0.76**	77.098	75.031	**-2.681**

Table 2.13 Table comparing 15 minute and 6 hour DOC export budgets. All units are in tC km^{-2} month^{-1} or tC km^{-2} year^{-1}

2.9 Discussion

The budgets show a wide variety of behaviour both between catchments and over time, with annual exports ranging between 10.4 and 89.9 tC km^{-2} year^{-1}. In simplistic terms, in order to demonstrate an improvement in DOC export from grip blocking the budgets from the blocked catchments would be lower than those for the unblocked catchments. This is not consistently the case. For 2004, the unblocked grip at Hexhamshire common (Hexham 2) shows a higher export than the two blocked catchments at that site, but the blocked grip at Cowgreen shows a higher export still. In 2003, the highest export at the Hexhamshire common site is from the blocked Hexham 3 catchment, whilst the Cowgreen catchment has the highest overall export in this year too, and the export from the unblocked Hexham 2 catchment is lower than either of these blocked catchments.

The export from the Hexham 1 catchment is consistently lower than the other three artificial catchments, but this is less clearly the case for the other recently-blocked catchment, Hexham 3. Hexham 3 is more comparable to the other grip catchments in terms of catchment size and hydrograph behaviour, whereas Hexham 1 is an extremely small, shallow catchment and dried up more frequently. This more frequent lack of flow in Hexham 1 could be due to the grip channel being much shallower (and therefore draining a smaller peat mass) than the other grips, rather than necessarily being due to a different response to blocking: the smaller size of Hexham 1 resulted more often in either a lack of flow or lack of sample, leading to lower calculated DOC export. Therefore the best comparison from the Hexhamshire common site is between the Hexham 2 and Hexham 3 grips.

With the exception of the Hexham 1 site, the DOC export by year varies inversely with catchment size, with smaller catchments having higher export per unit area. A larger catchment is more likely to have non-peat areas, which are likely to be less rich sources of colour than peat, contributing a diluting effect to the overall colour. There are also more likely to be opportunities within a larger catchment for removal of DOC, either by adsorption to other soils or aquifer materials or by mineralization during a greater stream residence time. Both of these are possible in the Widdybank catchment, which contains significant bedrock contact and shows (through a greater baseflow component than the grips, and higher conductivity) a groundwater influence. The catchment also contains some small non-peat areas, principally in the bed of the stream channels. Despite a common assumption that peatland catchments have minimal interaction with groundwater due to low hydraulic conductivity in the catotelm, recent studies have shown that this is not always the case – e.g. Branfireun and Roulet (1998) showed a substantial groundwater influence in the outflow of a peatland catchment in Ontario, Canada. However it seems intuitive that this will only apply in situations where there is sufficient hydraulic gradient to cause transfer from mineral layers to the overlying peat: in the Hexham and Cowgreen grips, the channels are only in the upper peat layers and the surrounding area is flat, so groundwater influence in these catchments would not be expected.

The same argument can be applied to Trout Beck, where the peat cover of the catchment above the sampling point is approximately 90% (ECN 2006a), compared to 100% peat cover at the Hexhamshire and Cowgreen catchments, and there are several kilometres of stream channel.

Relative to this inverse relationship between DOC export per unit area and catchment size, the export from Hexham 1 is anomalously low. However this could be due to the shallower nature of this catchment, as described above, as this means that the grip flows for less time between storms. Therefore, periods during and immediately after storms, when the all of the catchments are receiving low-DOC water both directly as precipitation into the channel and via overland flow, make up a greater proportion of the total time that Hexham 1 is flowing, compared to the other catchments. By this mechanism, a small shallow catchment such as Hexham 1 would be expected to have a greater influence from overland flow and rainfall – both sources of low-DOC water.

The DOC concentration of samples from Hexham 1 is generally lower also. During periods of no flow Hexham 1 often dried up entirely meaning that no sample was collected, and so the sample collection was effectively biased towards storm periods. This is in contrast to Hexham 3 and Cowgreen which even when they were not flowing dried up less often, such that samples were often taken of ponded water even where there was little or no flow contributing to DOC export. Therefore at Hexham 3 the average sample DOC concentration is high compared to Hexham 1, particularly in summer 2003 where Hexham 1 was dried up for long periods, and so the samples that were taken from Hexham 1 were of low average concentration relative to Hexham 3 which held ponded water. The same is true of Cowgreen, which held ponded water for long periods with no flow. Cowgreen shows particularly high sample DOC concentrations in the extremely dry period of summer 2003, due to this sampling of ponded water (Figure 2.11). Over these periods the DOC content of the water would become concentrated through evaporation and possibly also autochthonous production, without this affecting the export budget due to the lack of flow. The greater increase in DOC concentrations at Cowgreen during ponded periods does suggest greater autochthonous production at this site. Overall therefore, the concentration of DOC samples in itself provides little information as to the DOC export behaviour of the catchment, especially as it is confounded by artificially high concentrations measured in ponded water which by definition do not affect the net export budgets. Care must therefore be taken in interpreting the DOC export figures without taking account of the water yield, weighted for catchment area, in addition to the sample DOC concentrations. Nonetheless there is some evidence that concentrations in Hexham 2 during non-ponded periods – from January 2004 onwards – may be higher than in the other two Hexham grips, whilst Cowgreen is more subject to ponding and subsequent increased concentration (Figure 2.11). This possible difference in sample concentrations between Hexham 2 and the other Hexham sites is examined below and will be discussed further in chapter 3.

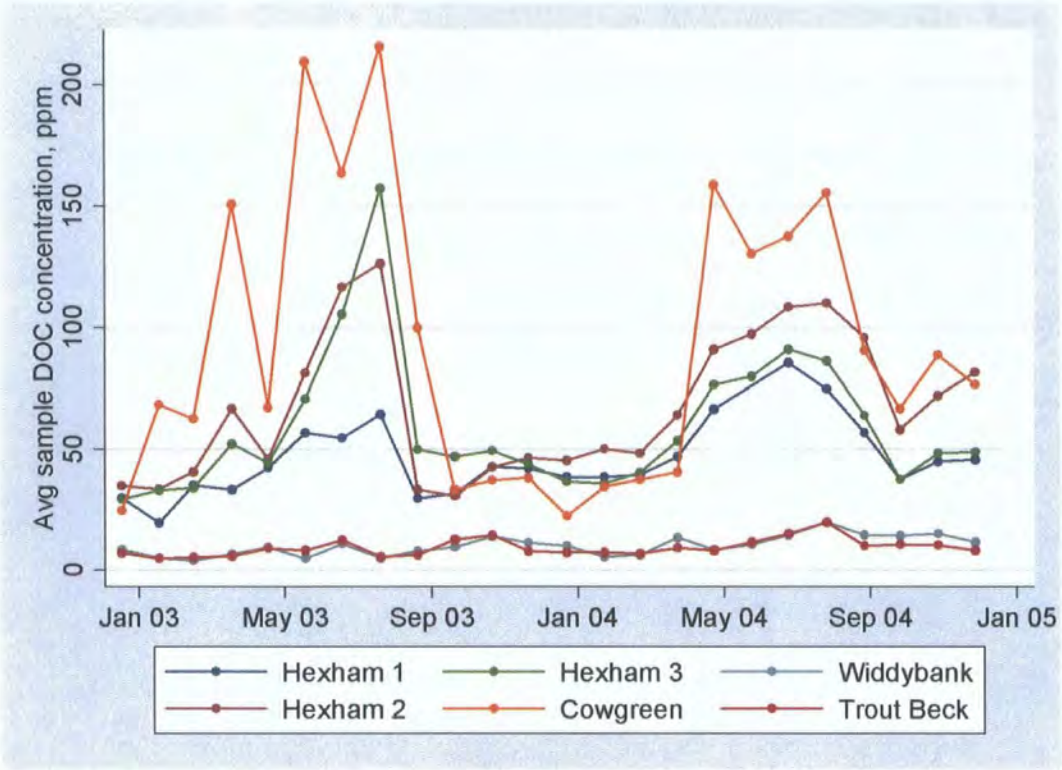


Figure 2.11 Average concentration of DOC samples, by month

Table 2.14 shows the results of each flow series, shown as cubic metres per square metre of catchment area per month (equivalent to runoff depth in metres). Corresponding results according to the 15 minute logged flow series where available at Hexham 2 and Widdybank are also shown. Total estimated runoff depths from the 15 minute and 6 hour data are extremely similar at both Hexham 2 and Widdybank, further illustrating the minimal increase in error from using the coarser time series.

Differences in the water yield, particularly at the Hexham sites where the rainfall may be assumed to be the same (the catchments are immediately adjacent) implies that the catchments are exhibiting different hydrological behaviour. To examine the effect of this on the DOC export budgets, Figure 2.12 plots monthly DOC export against the monthly water yields for each catchment. Significant relationships ($P<0.05$) are observed for each catchment. Details of these relationships obtained by least-squares regression fits are shown in Table 2.15.

Two main behaviours are illustrated by Figure 2.12. Firstly, there are substantial differences between sites in the relationship between water yield and DOC yield, and these differences suggest a grouping of sites by treatment type. The gradient of the relationship is lowest for the pristine sites Trout Beck and Widdybank, higher for the three blocked grips Hexham 1, Hexham 3 and Cowgreen, and is highest of all for the open grip Hexham 2. The coefficient of the relationship is not significantly different within each of the treatment groups ($P<0.05$) but is significantly different ($P<0.05$) between groups (Table 2.15).

Since both terms in these relationships are dependent on water export, the differences in the gradient of each relationship effectively describe differences between sites in the exported DOC concentration, illustrating that there are differences in sample concentration between treatments that are not due simply to changes in ponded water. That is, sample concentrations vary between treatment types even when the confounding effect of ponding is accounted for. This confirms that differences in the concentration of the *export* from each site, as well as in the area-weighted carbon budgets, are significant between treatment groups but not within treatment groups. This may imply that each catchment treatment type is exhibiting a different behaviour; for a given water yield the pristine catchments have a far lower DOC export than the gripped catchments, and of the gripped catchments the unblocked catchment has the highest DOC export for a given water yield.

However, before it can be claimed that the DOC export from the catchment soil is different between sites, the size of the catchments should also be considered. The pristine catchments are much larger than any of the grip catchments, which may suggest that there is a scale effect, with the larger pristine catchments exporting less DOC than may be expected. This represents losses in DOC that are likely to be due to adsorption or mineralization of the DOC, a process that does not have chance to occur in the smaller gripped catchments. This suggests that it may not be appropriate to make direct comparisons between the small single drain catchments and the larger catchments. However, taking the grip catchments alone this scale effect is not observed: Hexham 2 is the largest of the grip catchments yet it exhibits the highest DOC export for a given water yield of any of the grips (Figure 2.12). Therefore considering the grip catchments, there do appear to be differences which are not explained by size and subsequent in-stream DOC removal.

In summary, the lower DOC export for a given water yield in the pristine catchments may to some extent be due to DOC loss within the catchment. Nonetheless, the DOC export per unit water yield from the unblocked grip is significantly higher ($P<0.05$) than from the blocked grips and this does lend weight to the hypothesis that grip blocking can decrease DOC export, but in itself offers no evidence as to how the blocking process decreases DOC export.

The second main behaviour illustrated by Figure 2.12 that should be considered is the fact that for all sites a positive relationship exists between water yield and DOC yield, even without consideration of the differences between sites, and that these relationships appear to be approximately linear.

Based on these strong linear relationships, it can be suggested that reduction of water yield should be a key goal of a grip blocking programme. If, conversely, the relationships in Figure 2.12 were convex, with the gradient tailing off for higher values of water yield, this would imply that during months of high flow the DOC supply is exhausted; in this case blocking programmes designed primarily to reduce water yield would not be recommended unless they reduced water yield to a point where the relationship with DOC export was stronger. The high proportion of the variation in the DOC export that is explained by changes in water yield, particularly at the Hexhamshire Common site (Table 2.15; R^2 column) shows that water yield from a catchment is a key driver of the DOC export, with decreased water yield being a key driver of decreased DOC export. This is intuitive given the linearity of the relationships, with water yield being included on both axes, but if the relationships were not linear then decreasing the water yield would not necessarily be useful.

The relationship is particularly strong at the grip sites, which is equivalent to saying that, particularly at Hexham 1 and Hexham 3, the concentration (gradient of the relationship) is relatively invariant compared to Widdybank and Trout Beck, and is therefore the main factor controlling export. At the Teesdale sites, the lower R^2 may imply that the behaviour is more complex, but equally the steeper gradient at Hexham 2 compared with the blocked grips does illustrate that average export concentrations are lower in the blocked grips, but still higher than the pristine sites.

Overall, therefore, these data do provide evidence to support the hypothesis that artificial drainage increases DOC export and that grip blocking may be of use in reducing DOC export. The differing gradients of the relationships between treatment types do suggest that grip blocking reduces net exported DOC concentration, but the apparent linearity of the relationships and the high proportion of the variance explained in the Hexhamshire grip sites also suggest that the primary goal and function of a grip blocking programme should be to reduce catchment water yield, and blocks should be designed with this aim in mind.

Month	Hex 1 yield	Hex 2 yield (15 min)	Hex 2 yield (6hr)	Hex 3 yield	Cowgreen yield	Widdy yield (15 min)	Widdy yield (6hr)	Trout Beck yield
10/02	0.038		0.13	0.152	0.005			
11/02	0.086		0.2	0.293	0.078			
12/02	0.12		0.191	0.418	0.239	0.353	0.34	
01/03	0.130		0.144	0.387	0.381	0.672	0.673	0.071
02/03	0.015		0.011	0.042	0.058	0.247	0.247	0.097
03/03	0.071		0.049	0.191	0.139	0.304	0.304	0.072
04/03	0.021		0.015	0.019	0.047	0.068	0.067	0.031
05/03	0.044		0.136	0.063	0.165	0.383	0.381	0.133
06/03	0.010		0.022	0.013	0.014	0.014	0.013	0.016
07/03	0.014		0.036	0.021	0.027	0.1	0.100	0.066
08/03	0.001		0.003	0.002	0.003	0.012	0.013	0.127
09/03	0.011		0.031	0.027	0.028	0.054	0.056	0.048
10/03	0.016		0.011	0.028	0.019	0.104	0.102	0.069
11/03	0.044		0.069	0.098	0.135	0.483	0.472	0.175
12/03	0.078		0.165	0.205	0.166	0.454	0.457	0.208
01/04	0.102	0.244	0.229	0.281	0.699	0.643	0.645	0.263
02/04	0.116	0.151	0.155	0.327	0.481	0.428	0.440	0.156
03/04	0.080	0.089	0.086	0.203	0.257	0.296	0.296	0.133
04/04	0.074	0.046	0.043	0.139	0.120	0.19	0.188	0.093
05/04	0.022	0.019	0.018	0.016	0.037	0.031	0.030	0.032
06/04	0.024	0.049	0.049	0.041	0.021	0.084	0.083	0.061
07/04	0.023	0.029	0.028	0.023	0.022	0.121	0.120	0.079
08/04	0.078	0.238	0.211	0.104	0.245	0.641	0.653	0.359
09/04	0.021	0.056	0.052	0.035	0.036	0.161	0.163	0.164
10/04	0.154	0.314	0.283	0.370	0.242	0.661	0.644	0.221
11/04	0.057	0.1	0.094	0.109	0.045	0.286	0.287	0.205
12/04	0.080	0.16	0.160	0.174	0.079	0.07	0.063	0.188

Table 2.14 The total runoff from each catchment by month.
Depths are in m. Shaded cells indicate periods of missing data. Hex = Hexham; Widdy = Widdybank

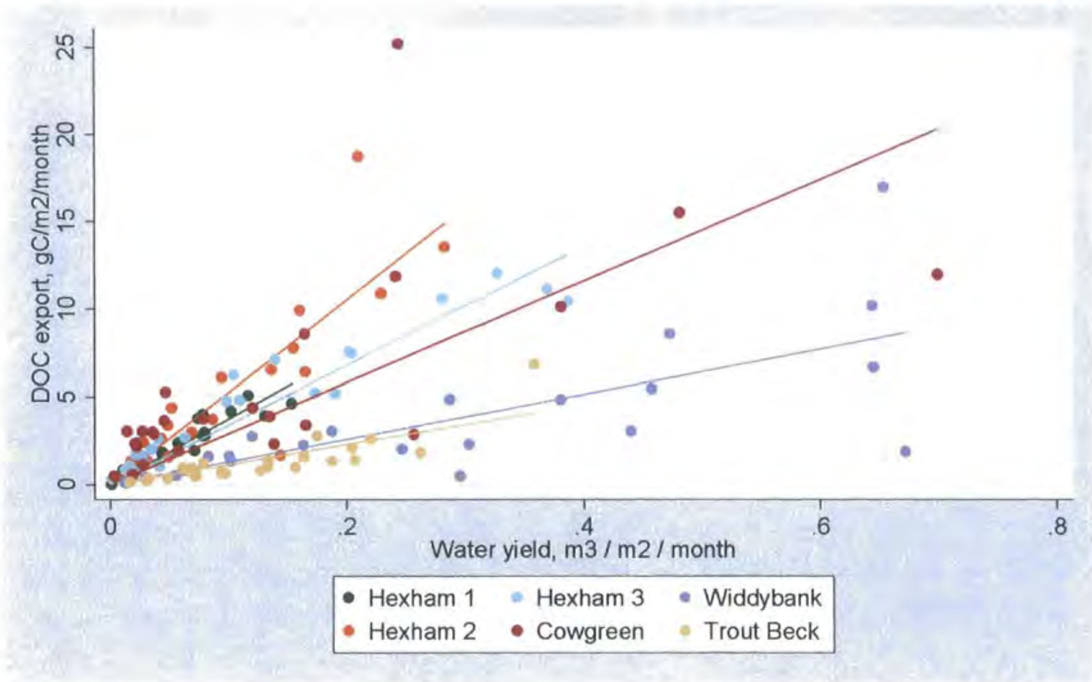


Figure 2.12 Water yield vs. DOC yield by month for each catchment. Water yields calculated from 6hr flow series.

	N	R^2	*Slope*	*Slope Std err*	*Slope 95% CI*	*Constant*	*Constant 95% CI*
Hexham 1	23	0.85	32.27	2.96	±6.17	0.46	±0.43
Hexham 2	24	0.77	51.52	5.99	±12.42	0.18	±1.45
Hexham 3	24	0.92	29.77	1.85	±3.83	0.99	±0.65
Cowgreen	24	0.43	22.01	5.40	±11.21	2.39	±2.48
Widdybank	24	0.56	13.09	2.49	±5.16	-0.10	±1.80
Trout Beck	24	0.72	13.96	1.84	±3.82	-0.45	±0.58

Table 2.15 Details of the relationships in Figure 2.12 between monthly DOC and water yields for each catchment

The implication of these results is that although the unblocked grip exhibits the highest DOC export concentration, the mitigating effect of grip blocking on DOC export may not necessarily be for the reason originally suggested – restoration of water table levels – at least not through the hypothesised mechanism of limiting production. The aerobic theory of DOC production proposes that DOC production is increased by temporary or permanent lowering of the water table and increasing of the aerobic zone, whilst the enzyme latch theory implies that once this process has taken place the effects may last for a long period. Therefore, according to the hypothesis, the lowering of the water table by grips would increase production and is the primary mechanism by which drainage would increase DOC export, which may then remain high even if the water table is restored through grip blocking.

The results of this study do not offer evidence to support this idea, with no evidence that DOC supply for export is exhausted in any month. This suggests that DOC yield is affected primarily by water yield, rather than by water table levels either antecedent or present. These data therefore suggest that DOC export is not supply-limited and that the production of DOC is fast on the inter-event timescale. However it should be recognised that the gradient of the relationships (representing export concentration) does vary between sites and so water yield is not the only control on export; further analysis of how this varies between blocked and unblocked sites is presented in chapter 3.

Evidence to support the suggestion of water yield being the main control is provided by Lumsdon et al (2005), who studied DOC partitioning into the soil solution in organic soils. They suggested that seasonal variations in DOC solubility, rather than DOC production, are sufficient to explain the observed variations in DOC concentrations and DOC production need not therefore be assumed to be supply-limited. Whilst there is a seasonal variability in concentration and this may indeed be due to changing biological activity – acting through seasonal factors affecting biological activity such as temperature changes – these variations operate by affecting the solubility of DOC rather than production rates. Periods of high DOC export are initiated by changes in the partitioning of DOC from hydrophobic to hydrophilic, more soluble, fractions (Lumsdon et al, 2005).

This study supports the model of Lumsdon et al (2005) by showing that the DOC export depends to a large extent on catchment water yield. This is as would be expected if DOC production was assumed not to be limited, but rather solubility was limited and variable with seasonal changes, possibly including water table fluctuations which may be caused by drainage as well as drought. Following this work by Lumsdon et al (2005), more studies are required with higher resolution DOC sampling across storm events to assess the extent to which DOC production is indeed fast on an intra-event timescale, in order to monitor the change in export concentration across individual storm events in greater detail.

Study authors	*Type of catchment*	*Location*	*Runoff*	*Export (tC km^{-2} yr^{-1})*
Mulholland (1981)	Swamp	North Carolina, USA	485	21
Naiman (1982)	Boreal forest	Quebec, Canada	570-1640	2.5-48.4
McKnight et al (1985)	Bog	Thoreau's Bog, MA, USA	240	8.4
Moore (1987)	Subarctic peatland	Quebec, Canada	302-389	1.1-1.9
Collier et al (1989)	Wetlands	Westland, New Zealand	1120-1104	28.7-37.8
Moore (1989)	Forested Wetland	New Zealand	137-1755	8-21
Moore and Jackson (1989)	Forested	Larry River, New Zealand	1023-1253	30.6-43.8
Urban et al (1989)	Various peatlands	Minnesota, USA and Orsario, Canada	224-1410	3-4
Koprivnjak and Moore (1992)	Subarctic fen	Quebec, Canada	111	1.2
Gorham (1995)	Northern peatland	?	N/A	20
Carroll Crill (1997)	Fen	New Hampshire, USA	1071	3.4
Scott et al (1998)	Upland peat	North Pennines, UK	798-1799	7-15
Elder et al (2000)	?	Wisconsin, USA	170-390	<26

Table 2.16 Summary of DOC export and runoff measurements in the literature (Adapted from Fraser et al, 2001)

The budgets calculated in this study are generally high compared to others in the literature. Table 2.16 summarises a review by Fraser et al (2001); other examples include Hope et al (1997a): 0.8 – 10.3 kg C km^2 yr^{-1}; Hope et al (1997b): 1.3 – 11.5 tC km^2 yr^{-1}; and Billett et al (2004): 11.5 – 27.0 tC km^2 yr^{-1}.

Fraser et al (2001) claim that DOC exports of > 15 tC km^2 yr^{-1} are unrealistic across large areas of northern peatlands taken as a whole, and in particular for low-relief peat-dominated catchments such as these. However they base this claim on limitations induced by runoff quantity rather than concentration, stating: "*assuming DOC concentration in export water is 30-40mg l^{-1}, ~375-500 mm yr^{-1} of runoff is required to yield 15 gC m^{-2} yr^{-1}*" (Fraser et al, 2001). The objection to higher exports is based on the grounds that "*runoff of this magnitude is....unrealistic in most places with peatlands*" (ibid.) However, the concentration figures used by Fraser et al (2001) are in agreement with those found in this study, and moreover runoffs of the magnitude quoted are far from unrealistic in North Pennine catchments: for example, Holden and Burt (2003b) found a runoff ratio of 82% in a catchment with mean annual rainfall of 1982mm. It is therefore not surprising to find that exports from the catchments in this study are higher than those found by Fraser et al (2001) or elsewhere in the literature from sites with lower precipitation / runoff, supporting further a view that differences in DOC export between catchments are in fact primarily dependent on differences in catchment water yield.

In summary, therefore, the results presented here do not specifically support the hypothesis that drain blocking is a successful strategy to reduce the DOC that is produced and available for export from a catchment. Whilst there are seasonal changes in concentration and export at each site, these can be at least partially explained by the model of Lumsdon et al (2005) whereby the key driver of seasonal change is variation in solubility. Meanwhile there is nothing in the data of this study to refute the hypothesis that the differences in export that are observed between catchments are caused by anything other than differences in the hydrological – rather than DOC production – behaviour of the catchments. Drain blocking may therefore be a successful mechanism for reducing the DOC export of the catchments, but this may only be through changing the hydrological behaviour of the drains. Chapter 3 will analyse the behaviour of the drains in more detail in an attempt to test this hypothesis.

3 Similarities and differences in blocked and unblocked catchments

3.1 Introduction

Chapter 2 described a detailed monitoring campaign conducted on four moorland grips and a pristine natural peatland stream. The aim of the monitoring campaign was to produce DOC budgets for each catchment and to describe the results in terms of the blocking status of the grips, in order to assess the effect of grip blocking on DOC export. It was found that what variations there were in the DOC export between blocked and unblocked catchments were attributable more to differences in the runoff responses of the catchments than to differences in the flow paths or sources of DOC production.

This chapter provides a more detailed assessment of the differences between the grip sites in terms of several other characteristics of the catchment outflow. Four experiments were conducted based on further analysis of the samples described in chapter 2 and on several other monitoring campaigns which were also conducted at the sites.

Firstly (section 3.2), the same samples described in chapter 2 were analysed for pH and conductivity; the results of this are used to describe and compare each of the five catchments.

Secondly (section 3.3), two of the sites (Hexham 2 and Hexham 3) were instrumented with quasi-continuous conductivity monitoring for a period in summer and autumn 2004. The results of this monitoring are used to conduct hysteresis analyses to compare the intra-storm response of these two catchments in a way that is not possible with the less frequent sample-based data due to the extremely fast response times of the catchments.

Thirdly (section 3.4), a series of manual grab samples were collected on site visits throughout the period of the study. These samples were analysed for base metal cation content and the results used to conduct a Principal Components Analysis. The results of this are used to describe differences in water chemistry between the sites and then are analysed using an ANOVA method to assess for any statistically significant differences between the sites.

Finally (section 3.5), a tracer flow experiment was conducted specifically to test the hypothesis that there are differences between the blocked and unblocked sites. This consisted of the introduction of bromide and chloride tracers to the catchments, into the water table and onto the catchment surface. This was followed by an intensive sampling campaign of the grips at the catchment outlet points to compare the tracer response between the grips. Results from this experiment are presented and their implications and limitations discussed.

3.2 Relationship of pH vs. Conductivity at each site

The sampling campaign described in chapter 2 gathered samples from four peatland grip sites and one pristine peatland stream. Of the grip sites, 2 (Hexham 1 and Hexham 3) were blocked shortly after the start of the monitoring campaign, one (Cowgreen) was blocked in 1995, and one (Hexham 2) remained as an unblocked site.

In addition to analysing for DOC, the samples collected from these sites on an 8-hourly to daily sampling regime were also analysed in the laboratory for pH and conductivity. Prior to analysis, samples were refrigerated in the dark at 4°C, and analysed within 24 hours of collection. Conductivity has often been treated in peatland sites as a conservative property indicative of solute concentration (e.g. Schleppi et al, 2006). Over 800 samples were analysed from each site, and weekly rainfall data were also obtained from the ECN monitoring programme at Moor House (Sykes and Lane, 1996) for the same period. Results showing the relationships between pH and conductivity for each site are shown in Figure 3.1 and Table 3.1.

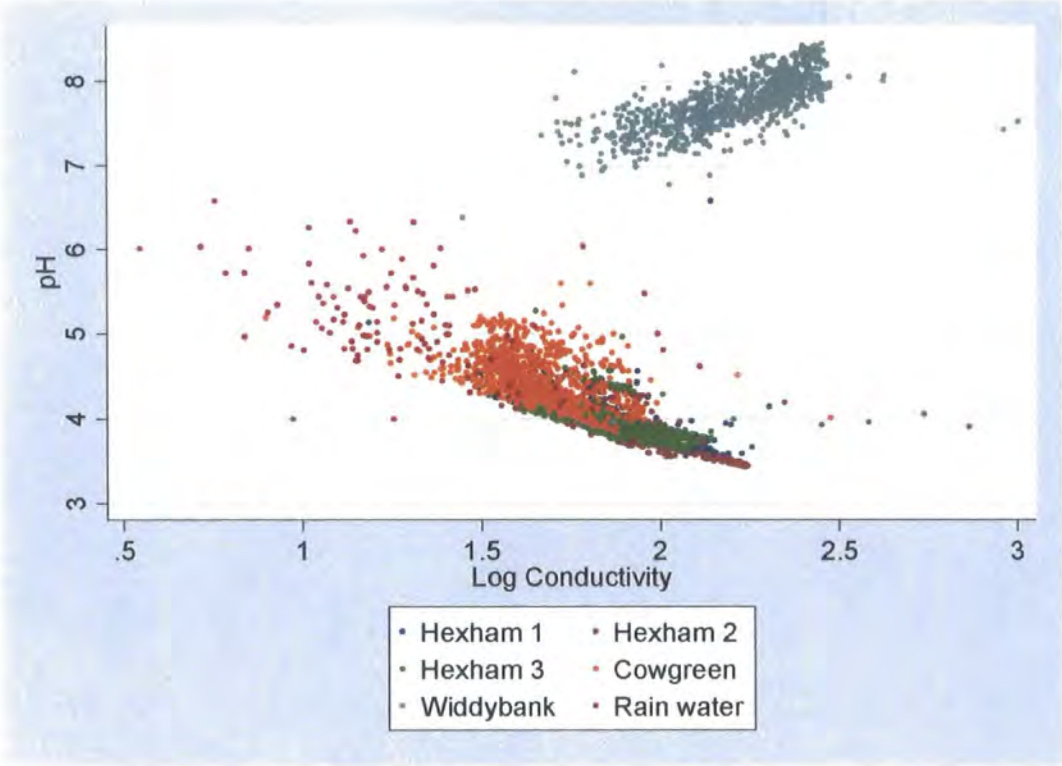


Figure 3.1 Plot of pH against Log(Conductivity) for all sites

The relationship between pH and conductivity was found to be linear for all sites when a log transform was applied to the conductivity data. The necessity for a log transform on the conductivity data is unsurprising, as pH itself represents the negative logarithm of H^+ ion concentration. The plot of pH against Log(Conductivity) reveals strong linear relationships for all sites (Figure 3.1). The relationship between pH and Log(Conductivity) is highly significant for each site including rain ($P<0.0005$); details of the fits are shown in Table 3.1. The trend for each grip and for rain is negative; that is, increased conductivity corresponds to decreased pH. The three Hexham sites and Cowgreen lie on similar trends, with the slopes of the trends for Hexham 1 and 2, Cowgreen, and rain showing no significant difference ($P<0.05$), whilst the slope of the trend for Hexham 3 is significantly shallower but still similar. The Widdybank trend is of opposite sign but otherwise not significantly different ($P<0.05$). The Cowgreen samples have somewhat more scatter around the trend than the other grips or Widdybank, with $R^2=0.22$. The fits between pH and Log(Conductivity) for all the grip sites have a similar y-intercept of around pH 6, comparable to the pH of water at equilibrium with the atmosphere. With conductivity assumed to be a conservative tracer, higher conductivity represents more concentrated samples. The similar trends of the grip sites and rainwater (Table 3.1) therefore suggest that in terms of pH and conductivity, there are not necessarily any different influences on either pH or conductivity between the grip sites and the decreasing pH / increasing conductivity trend could be seen simply as increasing concentration from rainwater.

Conversely, the Widdybank samples are of much higher pH and follow an entirely different trend with a positive relationship between pH and conductivity. The intercept term of the trend is however at a somewhat lower pH of 4.97. These differences can be explained by considering the nature of the Widdybank site which compared to the grips is a substantially larger catchment with a greater baseflow component. The baseflow component at Widdybank together with high Ca concentrations and higher conductivities at baseflow have been attributed (section 2.9) to a groundwater influence or surface limestone contact within the catchment. Such an influence would contribute to both increased alkalinity and conductivity in the baseflow, and the proportion of baseflow in the overall discharge is by definition greater at lower discharge values. Lower flows in the Widdybank catchment therefore lead to increased conductivity and pH in the runoff as the contribution of the groundwater / limestone source is greater. The lower intercept of the Widdybank trend can also be explained in terms of limestone contact and the subsequent greater presence of carbonic acid in the system.

Plotting pH against Log(Conductivity) for separate seasons (Figure 3.2) shows that the relationship between pH and conductivity is strongest throughout the autumn flush period; this is the period when the samples are most representative of catchment / peat processes, with few ponded samples and few taken when the catchments were frozen. Throughout winter and spring the Cowgreen samples appear to be more separated from the Hexham samples (with a lower range of conductivities at Cowgreen); however this is the period during which catchments are most likely to have been frozen and the distance between the Cowgreen and Hexham sites means that the difference may simply be attributable to one site being frozen at different times to the other.

The results for the grip sites shown here do not correspond as expected with examples from the literature which take into account the production of pH and / or conductivity within the peat. In particular Sjörs and Gunnarsson (2002) describe peat substances as tending to accumulate cations such as Ca^{2+} and Mg^{+} (responsible for increased conductivity) whilst releasing H^{+}. This implies the opposite trend occurring in the water, with water in contact with the peat showing decreased conductivity (Ca^{2+} concentrations) corresponding to decreasing pH (increasing H^{+} concentrations). Such a trend is observed in the data of Sjörs and Gunnarsson (2002) but is opposite to the trend of increasing conductivity vs. decreasing pH observed at the grip sites here. This implies that processes within the peat that would affect pH or conductivity are not strongly observed in these data, and backs up the explanation given above that the trend in these data is due simply to increased relative concentration from rainwater. The greater scatter observed in the Cowgreen data could indicate conflict between the two mechanisms: that is, simple increased concentration leading to a negative trend and processes as described by Sjörs and Gunnarsson (2002) adding some degree of positive trend. This explanation would correspond with the results in Section 2.7 and field observations which suggest there may be greater autochthonous production at Cowgreen.

	Overall						*R^2 by season*			
Site	N	R^2	Slope	Slope 95% CI	Constant	Constant 95% CI	Spring	Summer	Autumn	Winter
Hexham 1	908	0.62	-1.22	±0.062	6.25	±0.118	0.45	0.12	0.66	0.47
Hexham 2	966	0.66	-1.19	±0.054	6.14	±0.106	0.02	0.16	0.97	0.30
Hexham 3	1110	0.50	-1.00	±0.059	5.81	±0.110	0.60	0.36	0.70	0.13
Cowgreen	1010	0.23	-1.11	±0.126	6.31	±0.208	0.12	n/a	0.34	0.23
Widdybank	898	0.48	1.26	±0.086	4.97	±0.192	0.53	0.52	0.47	0.24
Rain water	157	0.22	-0.93	±0.340	6.36	±0.443	0.22	n/a	0.30	0.20

Table 3.1 Details of the relationships between pH and Log(Conductivity) for each site as shown in Figure 3.1.
Laboratory measurements. All overall regression coefficients significant with P<0.0005 and all season-wise coefficients with P<0.05 except n/a = not significant

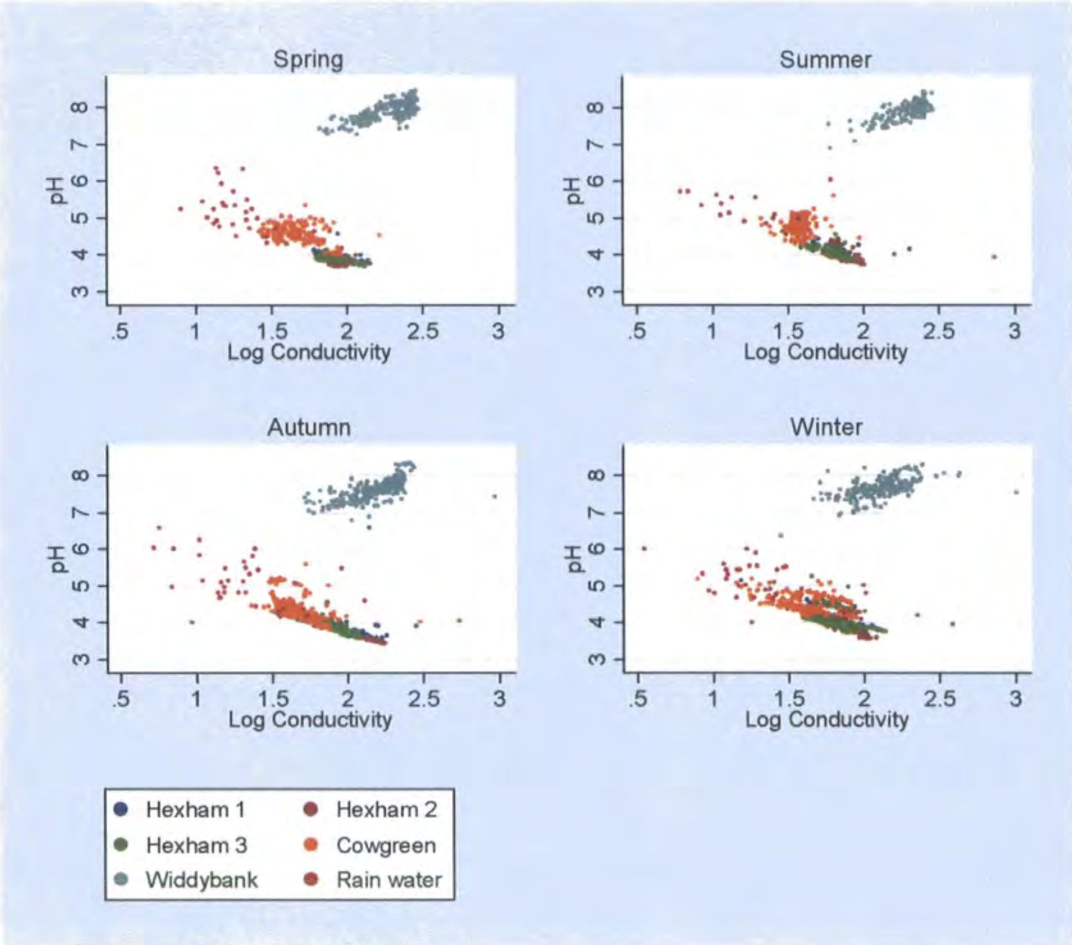


Figure 3.2 Plot of pH against Log(Conductivity) for all sites by season.
Spring = March-May; Summer = June-August; Autumn = September-November; Winter = December-February

In summary, the grip sites in this study show a relationship between pH and conductivity that can be best explained in terms of increasing concentration from a rainwater source, with minimal alteration of this trend by any form of production within or interaction with the peat. This is particularly true for the grips at Hexhamshire common. The behaviour of the Widdybank catchment is seen to be quite different to the four grips. Although the positive pH vs. conductivity trend at Widdybank is more in line with that found by Sjörs and Gunnarsson (2002) and may imply greater chemical interaction with the peat at Widdybank, there are also at least two water sources against only one in the grips, with the higher pH implying and conductivity suggesting a higher ionic strength that may be due to groundwater or limestone contact within the channel. In any case there are huge differences in the behaviour of the Widdybank catchment from the grips which demonstrate the difficulty of comparing it on a like-for-like basis with the grips; as the main aim of this study is to test the hypothesis that there are differences between blocked and unblocked grips, the Widdybank data were therefore not included in the remainder of the analyses in this chapter. Conversely the behaviour of the four grip sites is similar, especially among the three Hexham sites. This suggests that there are no differences between the grips such as differing acidities that cannot be attributed simply to conservative concentration from a single source water.

3.3 Hysteresis of the conductivity vs. flow response in Hexham 2 and Hexham 3

In addition to the manual measurement of conductivity on samples collected for the DOC monitoring programmes, (section 3.2), in May 2004 electrical conductivity probes were installed in the Hexham 2 and Hexham 3 drains. The probes were connected to the Campbell CR10X logger at the site and were temperature compensated to 25°C using internal routines in the data-logger before data storage. The probes were sampled every 10 seconds and average readings were stored every 15 minutes, providing a quasi-continuous conductivity record for these sites for the period May – November 2004. The probes were installed parallel to the direction of water flow in order to ensure the best response possible and were mounted on wooden posts at a depth of approximately 3cm below the base of the V-notch weir – this depth was chosen to ensure that the probes remained immersed as far as possible whilst being clear of silt at the base of the grip channels (Figure 3.3 and Figure 3.4).

Figure 3.3 Conductivity probe installation in Hexham 2

Figure 3.4 Conductivity probe installation in Hexham 3

Conductivity is a good proxy for ionic concentration (Meybeck et al, 1996) and as such rainwater would be expected to form a low conductivity end-member in most systems with more evolved waters throughout the system increasing in conductivity, albeit to an extent that will vary greatly depending on the geology of the system: the global average conductivity for pristine streams draining granite and gneiss catchments is 35 $\mu S\ cm^{-1}$, whilst for carbonate catchments the figure is 400 $\mu S\ cm^{-1}$ (Meybeck et al, 1996). Peat bogs are no exception, despite the fact that peat soil waters and small peatland drains or streams such as those in the present study do not generally have direct interaction with the geology. Theimer et al (1994) studied three Canadian peatlands and in each case found ionic strength and electrical conductivity to increase linearly with depth. Pearsall (1956) sampled surface waters from furrows, pools and main drainage outlets sited on transects which were approximately along the main drainage lines of two bogs in Sutherland and found a general increase in concentration along the transects with the highest conductivities being observed near the outflow.

In the context of this study it is therefore reasonable to take conductivity as an indicator of the depth of source waters that is observed in the grip channels. Since conductivity in a stream will also vary with time as the relative proportions of new and evolved waters vary, in order to identify differences between sites it is necessary to examine differences between sites in how the conductivity varies throughout a storm. This can be achieved through the use of conductivity / discharge hysteresis plots. The form of such plots depends on the timing and quantity of the release of higher conductivity soil waters relative to the input of new (rain) water: if the old water discharge peaks before the overall hydrograph then the plot of conductivity against flow will show a clockwise loop: conductivity / discharge is higher on the rising limb than the falling limb for all discharge values. In the opposite case, the loop is anticlockwise. Williams (1989) classified hysteresis types with reference to the relationship between suspended sediment concentration and discharge. According to this classification, Class 1 represents a linear relationship between concentration and discharge; Class 2 is a clockwise loop, Class 3 is an anticlockwise loop, Class 4 is a linear relationship with a loop at some point, and Class 5 is a figure of eight whereby the hysteresis is clockwise at one range of flow values, and anticlockwise at another.

With reference to these descriptions, a clockwise loop in the conductivity / flow data (Class 2) represents an initial flushing of "old" soil water which is then exhausted and becomes a less major part of the overall runoff as the storm progresses. An anticlockwise loop (Class 3) indicates that the early stages of the storm runoff are characterised by relatively unaltered new water, with the contribution of soil water increasing later. A figure of eight (Class 5) that starts anticlockwise and becomes clockwise at higher discharge could indicate an initial dominance of new water such as infiltration-excess overland flow, followed by an increasing proportion of subsurface flow as the peat surface wets up.

Analysis was conducted on the 15-minute timestep data as collected by the loggers. Whilst this was not a problem for Hexham 2 where a good logged flow record existed, at Hexham 3 the flow record had many gaps and so was modelled using the IHACRES techniques described in chapter 2. The modelled flow series for the entire monitoring period as described in chapter 2 was produced on a 6-hour timestep due to limitations in the modelling software, and this did not provide sufficient resolution for this analysis of intra-storm variations. However, it was found that the IHACRES model could in fact be successfully operated to simulate flow on a 15-minute timestep for shorter periods such as the 6 months of this dataset, and so a new 15-minute modelled flow series was produced for Hexham 3 for use in the following analysis.

3.3.1 General differences in grip water conductivities

The distribution of conductivity values during the monitoring period is shown in Figure 3.5, where the upper and lower box boundaries mark the 75th and 25th percentiles respectively and the centre line represents the median. Interquartile range (IQR) is defined as the difference between the 75th and 25th percentiles. Whiskers extend to the most extreme values which fall within the upper and lower adjacent ranges, which are defined as (75th percentile + 1.5*IQR) and

(25^{th} percentile – 1.5* IQR) respectively. This plot excludes readings taken when there was no flow in the grips (there was either ponded water or nothing in the grips during such periods) in order to minimise the effect of evaporative concentration that is not connected to runoff generation processes. The plot also shows for comparison the conductivity of weekly rainfall samples collected by the ECN at Moor House for the same period (Sykes and Lane, 1996).

The plot shows that conductivity in Hexham 3 was consistently lower than in Hexham 2, with a similar range of values. Since conductivity is expected to increase with depth in the peat profile as described above, the implication of this is that Hexham 3 represents shallower water on average than Hexham 2. However an alternative approach to understanding this could be that the water in the Hexham 3 drain simply contains a greater proportion of (relatively unaltered) overland flow, with no systematic variation in the source depth of the soil water component between grips.

Which of these explanations is correct can be understood by considering the differences in conductivities between the grips under both storm flow and low flow conditions. During low flow, when there has been no recent precipitation, there would be no overland flow and so differences between the grips would be less than at high flow, if the second explanation is correct. Figure 3.6 shows the conductivities in the grips over the same period for the occasions when there was no flow (only ponded water) in the grips. The range of conductivity in each grip is smaller, as would be expected, but the general pattern of higher conductivity in Hexham 2 is unchanged. This suggests that the first explanation is correct: the lower conductivity in Hexham 3 is not due to a higher proportion of overland flow in that grip (which would not be observed in Figure 3.6), but rather to Hexham 3 representing shallower soil water than Hexham 2.

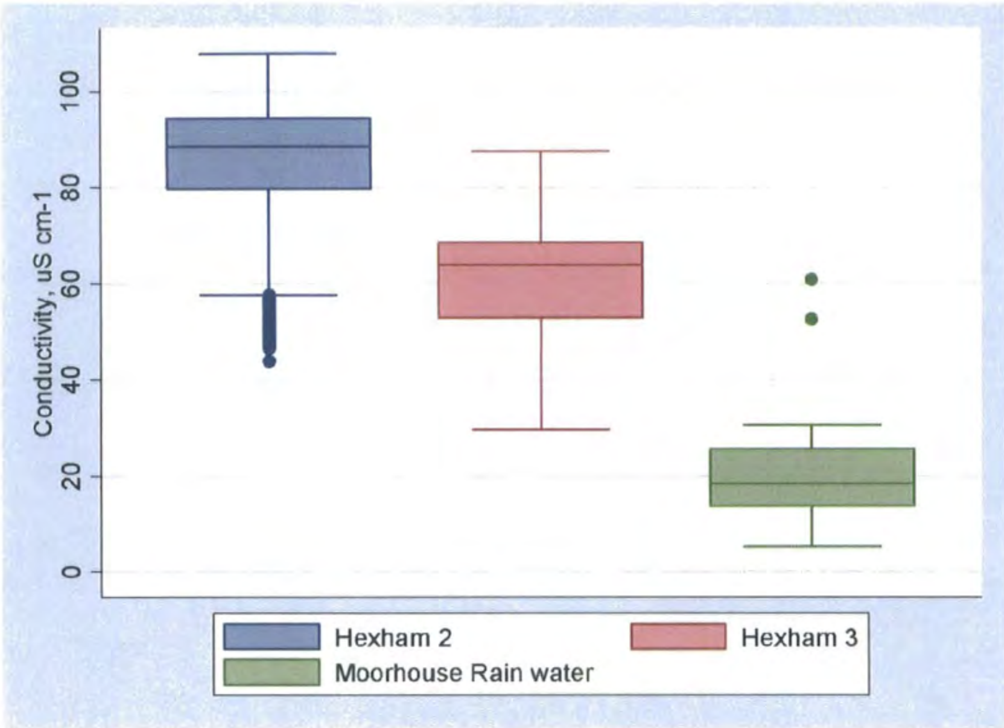


Figure 3.5 Conductivity in Hexham 2, Hexham 3 and rainwater over the period of monitoring, excluding ponded water

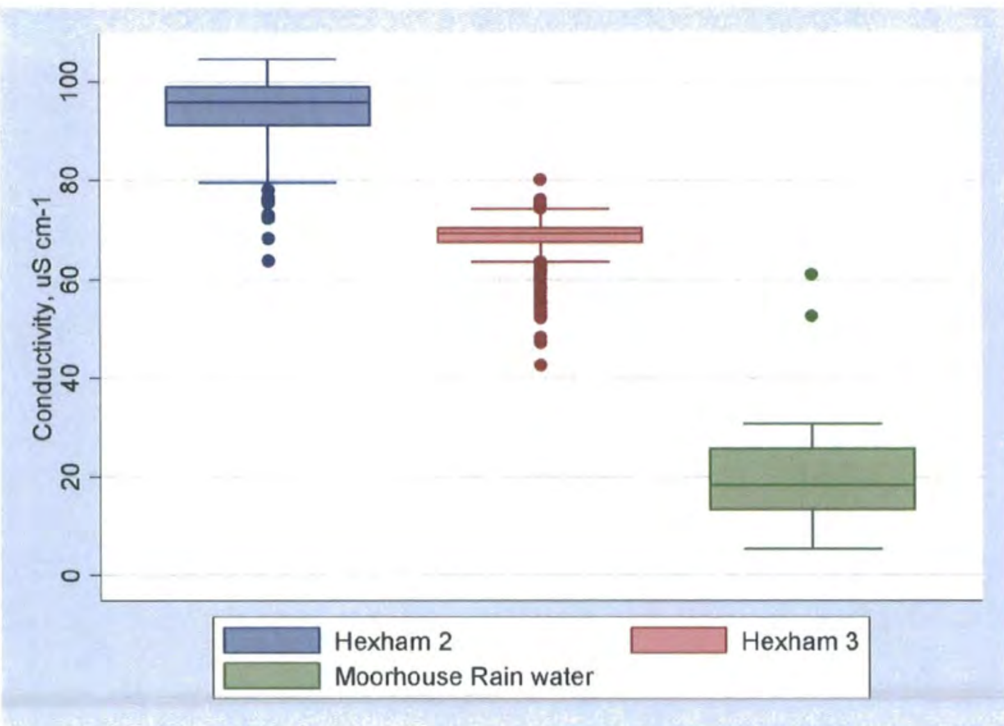


Figure 3.6 Conductivity in Hexham 2, Hexham 3 and rainwater over the period of monitoring, for ponded water only

3.3.2 Hysteresis analysis

Although there are systematic differences in the conductivity of Hexham 2 and Hexham 3, these appear to be linked only to the depth of soil water that is represented in the grips and not necessarily to any differences in flow pathways. To test this further the conductivity / flow hysteresis plots for a number of storm events were examined. Events were selected where the hysteresis loops showed the most recognisable forms. Occasions where the hysteresis form was unclear included very small events (which may have been due to insufficient flow in the event to fully flush standing water from the channels) and composite events (although one such period of several closely spaced events was analysed for comparison). The hydrographs and hysteresis plots for each of these events are shown in Figure 3.8 – Figure 3.21. All events are towards the latter half of the monitoring period as earlier in the summer there were no suitable events.

The events on the 12th-13th August and the 19th-21st August were similar as they were both substantial events which took place shortly after much larger events, so the catchments would already have been wet. Both events show Class 2 hysteresis in each catchment (Figure 3.9 and Figure 3.10), suggesting that the early stages of the event were dominated by subsurface flow displacing relatively high-conductivity waters – infiltration- or saturation-excess overland flow did not occur in either grip. Although the change in conductivity throughout each event was greater in Hexham 2, the conductivity in Hexham 2 did not drop as low as in Hexham 3, suggesting that even at peak flows the water in Hexham 2 still came on average from deeper sources than in Hexham 3. The relative responses of the grips seem to be similar in each of these events.

The event on 22nd-23rd September was much smaller and additionally was not so well separated from antecedent events. Accordingly the form of the hysteresis loops (Figure 3.12) is less clear, with more noise in the data due to the smaller magnitude of the changes. Hexham 3 shows Class 3 hysteresis whilst Hexham 2 shows Class 5 hysteresis with an anticlockwise loop at higher flow values that becomes clockwise at the end of the event, suggesting overland flow becoming dominant at the peak of the event in Hexham 2, but prevailing earlier in the event in Hexham 3.

The hysteresis form for the event on 2nd-3rd October (Figure 3.13) is somewhat confused due to the two-peaked nature of the event (Figure 3.11). However, the general form is Class 3 hysteresis at each site, with no real differences between the sites. The hydrograph for Hexham 2 shows a dry period of approximately 10 days prior to this event and this may well have been sufficient for the upper layers of the peat to dry sufficiently to delay re-wetting and lead to infiltration-excess overland flow during the early stages of the event. It should be noted that the Hexham 3 hydrograph shows several small events during this "dry" period – it seems likely that the IHACRES model is over-responding to small rainfall inputs during times when the catchment is dry, and this does suggest that the event on 2nd-3rd October should be interpreted with some caution.

The event on 6th-7th October (Figure 3.15) was moderately large and of high intensity, and unusually followed a period of approximately two days when there was a substantial level of sustained flow in the grips. It is therefore not surprising that both sites show some degree of Class 2 hysteresis, but this is much more apparent in Hexham 3 – the loop for Hexham 2 is very narrow. This suggests that the supply of high-conductivity water at Hexham 2 is more constant and is not exhausted so early in the event.

The events on 13th-14th October (Figure 3.16) and 14th-15th October (Figure 3.17) were immediately consecutive and were extremely similar both in terms of rainfall input and flow response, emphasising the flashy nature of the catchments – the flow response from the second event was not greatly higher as it would be if the water table was higher at the start of the second event than the first. The Class 3 hysteresis response of Hexham 2 is similar between the events suggesting an overland flow component dominating initially, followed by runoff from the soil. The loops are almost closed with both post-event and pre-event values being similar for both conductivity and flow, and the similarity of the loops for the two events at Hexham 2 shows that high conductivity waters were not exhausted. Hexham 3 displays similar behaviour to Hexham 2 for the first event, but the behaviour in the second event is quite different: although there is a small Class 3 loop partway through the event, this is overlain on a generally unclear hysteresis form in which the key observation is that conductivity after the event is lower than the pre-event values. The suggested reason for this is not differing flow pathways, but rather to do with the large pools in the Hexham 3 channel behind the blocks (Figure 3.7). It seems possible that these two events in conjunction were sufficient to flush these pools through with new low conductivity water, resulting in lower grip conductivity when flow from leakage round the blocks becomes dominant as the hydrograph recedes.

Figure 3.18 encompasses several composite events representing a period of sustained high flow from 15th-19th October. Since there were numerous flow peaks the hysteresis form is too complicated to analyse in detail (although most flow peaks do appear to be represented by Class 3 loops) but it is included as this demonstrates the general decrease in conductivity over a much larger range (note different y scales between figures) over a sustained wet period. This seems likely to be caused by exhaustion of high conductivity waters from the soil layers that are dominating flow, and although the pools in Hexham 3 do seem to provide the potential for a step change in outflow conductivity (see above) the effect of this is small compared to the overall exhaustion effects that are observed in both grips and which cause a larger decrease in conductivity throughout wet periods which gradually recovers if there is a subsequent dry period.

Effectively this means that for both sites there is a tendency in large events to generate a Class 3 hysteresis loop (through overland flow followed by subsurface flow dominance) which is itself superimposed on a much larger Class 2 hysteresis form due to flushing out of the soil waters over sustained wet periods – the first part of such a Class 2 form is what is observed in Figure 3.18. The event-scale loop is not always Class 3 (as demonstrated by many of the Class 2 loops discussed above); which form this takes is likely to be controlled by peat surface conditions affecting infiltration capacity.

Based on these analyses, although there are some differences between the grips in their flow path response to storm events, these can all be explained in terms of Hexham 2 sampling deeper and more sustained soil water sources, giving it a higher concentration that is sustained over longer periods. This is in contrast to a difference between the relative contributions of overland and subsurface flow within an event that would be expected if grip blocking in Hexham 3 changed flow paths substantially by raising the water table. In fact both catchments receive overland flow and the proportions of this do vary depending on the size of an event and the antecedent conditions, but there is nothing to indicate that this is higher in Hexham 3. The role of ponded water in Hexham 3 caused by the substantial ponds that formed behind the grip blocks may provide a "reservoir" of high conductivity water that complicates the behaviour of this site, depending on whether the size of an event is sufficient to flush the pools through with new water, and how quickly the ponded water is released compared to overland flow arriving in the channel below the grips and ponds.

Figure 3.7 Pool behind a grip block in Hexham 3 (photo is taken from the block).

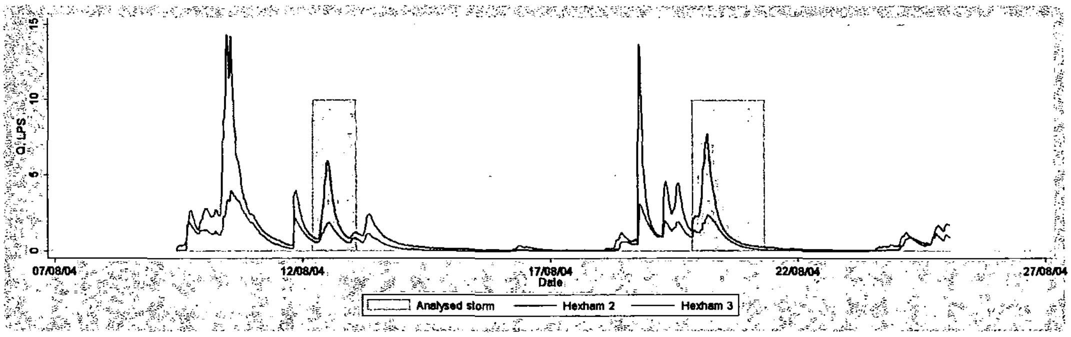


Figure 3.8 Hydrograph showing events on 12/08/04 and 19/08/04

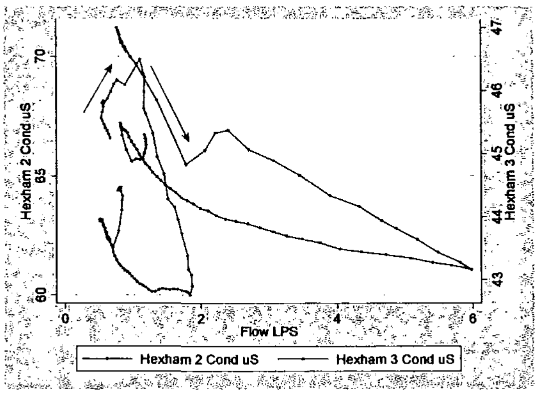


Figure 3.9 Event on 12/08/04 - 13/08/04. Rainfall = 16.2mm

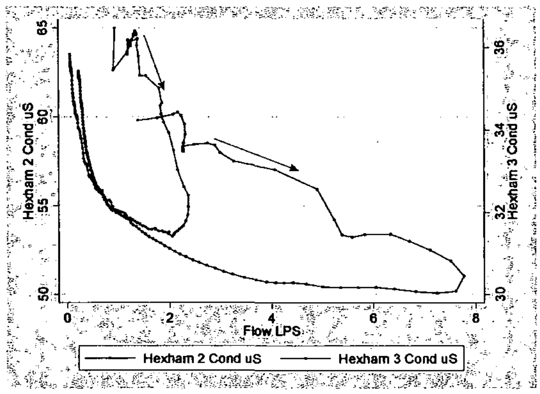


Figure 3.10 Event on 19/08/04 - 21/08/04. Rainfall = 19.6mm

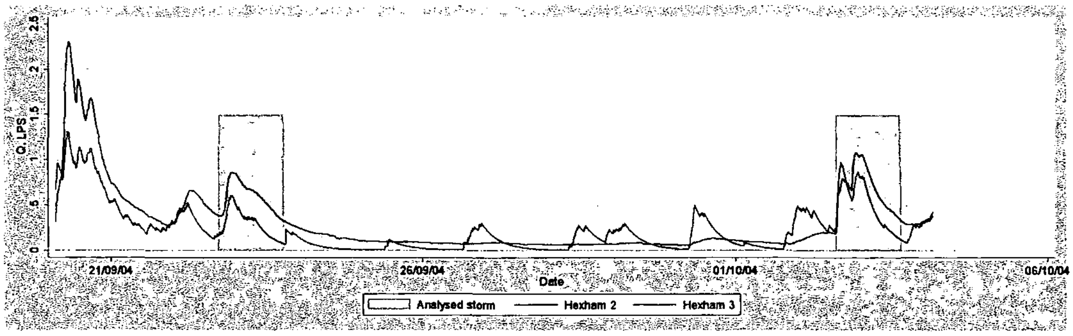


Figure 3.11 Hydrograph showing events on 22/09/04 - 23/09/04 and 02/10/04 - 03/10/04

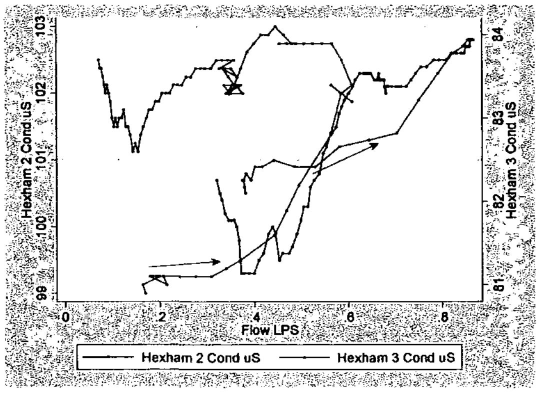


Figure 3.12 Event on 22/09/04 - 23/09/04. Rainfall = 5mm

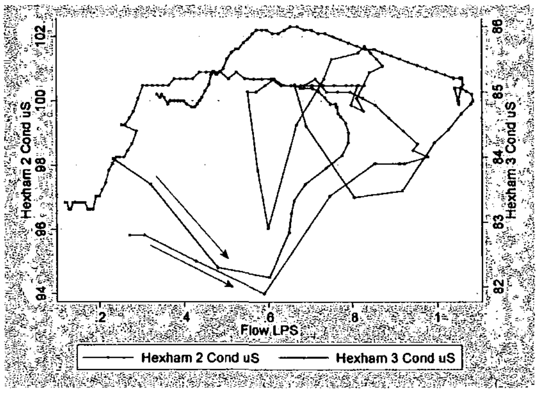


Figure 3.13 Event on 02/10/04 - 03/10/04. Rainfall = 8.2mm

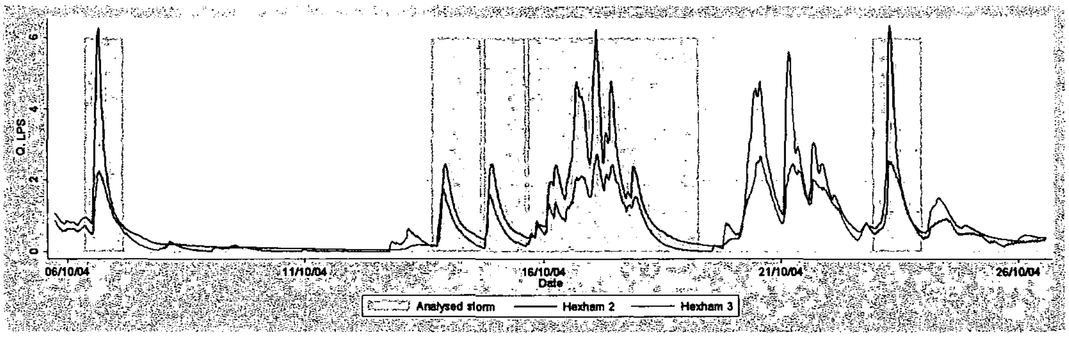


Figure 3.14 Hydrograph showing events on 06/10/04-07/10/04; 13/10/04-14/10/04; 14/10/04-15/10/04; 15/10/04-19/10/04; and 22/10/04-23/10/04

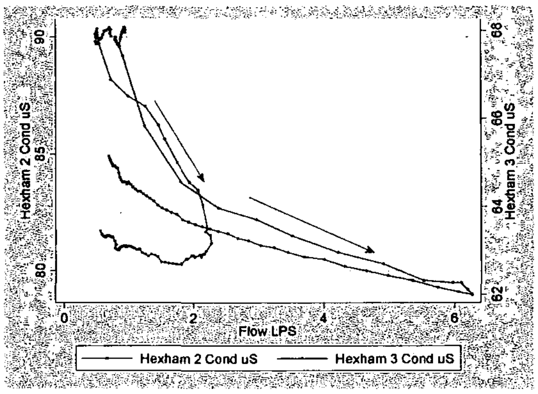


Figure 3.15 Event on 06/10/04 - 07/10/04. Rainfall = 14.2mm

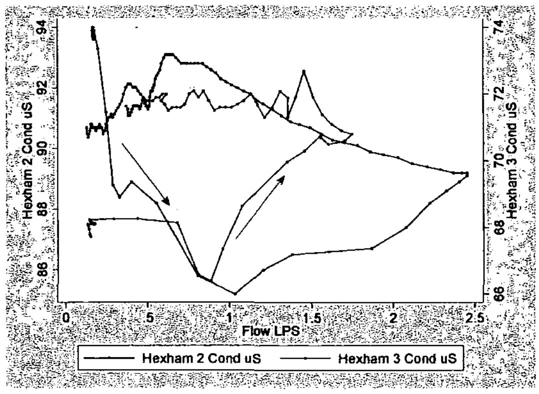
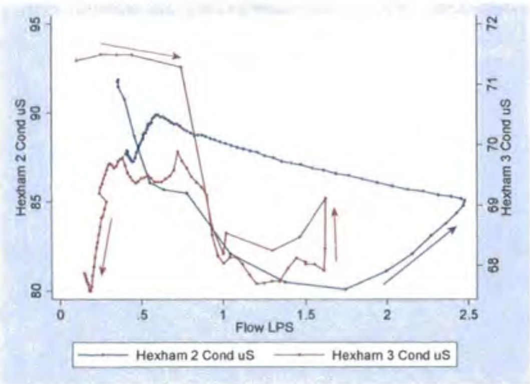


Figure 3.16 Event on 13/10/04 - 14/10/04. Rainfall = 8.8mm



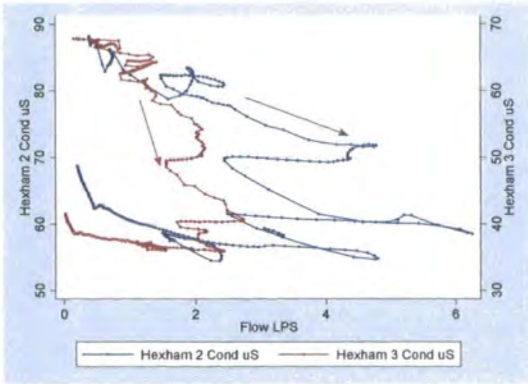


Figure 3.17 Event on 14/10/04 - 15/10/04. Rainfall = 9.4mm

Figure 3.18 Overall behaviour of several events 15/10/04 - 19/10/04. Rainfall = 46.8mm

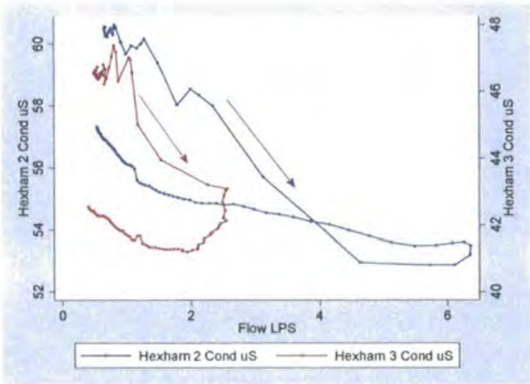


Figure 3.19 Event on 22/10/04 - 23/10/04. Rainfall = 13.6mm

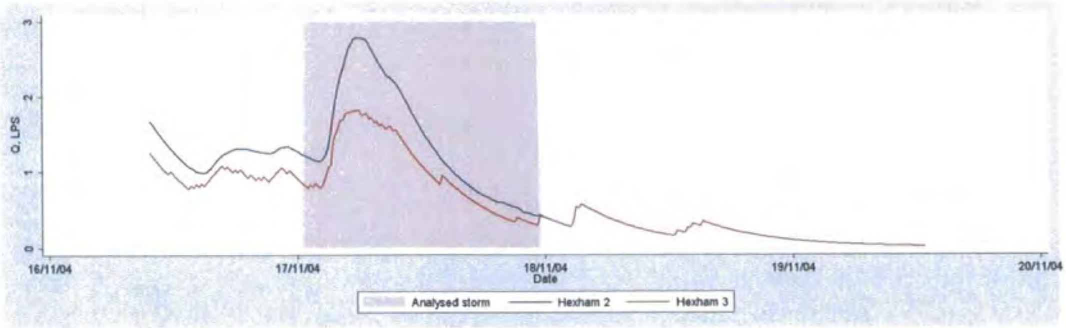


Figure 3.20 Hydrograph showing event on 17/11/04

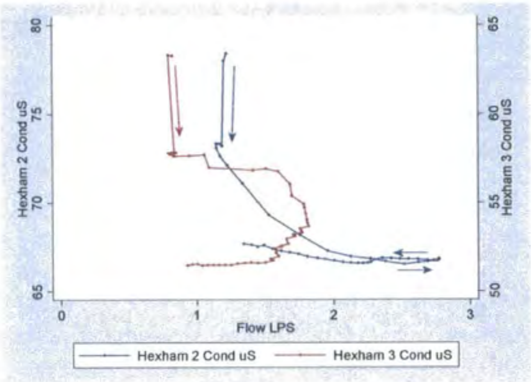


Figure 3.21 Event on 17/11/04. Rainfall = 7.4mm

3.4 Multivariate analysis of catchment export

3.4.1 Background to multivariate techniques

3.4.1.1 General introduction

Principal components analysis (PCA) examines multivariate datasets where there are correlations between some or all of the variables. By seeking patterns in the correlation or covariance structure new variables or components are identified representing as much as possible of the variation in the dataset in a smaller number of variables: if there are *m* variables in the dataset, the goal is to find a set of *n* uncorrelated components where *n* is substantially less than *m* but which still explain a large proportion of the variance in the original dataset. PCA is therefore a data reduction or simplification technique because a small number of components explain a larger proportion of the variance in the dataset than could be explained by any combination of the same number of original variables. Once identified the components can then be transformed into the terms of the original variable set and used for further analysis, as the output for each of the n components is a coefficient or loading for each of the variables in the original dataset, so each observation can be assigned a score for each retained component by multiplying the observed value for each variable by the loading for that variable and component.

Factor analysis (FA) is similar in concept to and an extension of PCA. In PCA the loadings for each component are selected to maximise the total variance in the original data that is explained by each component. This may or may not result in components that are easy to interpret in terms of underlying causes. If a component had high loadings on variables that could be explained by a similar source and negligible loadings on all other variables, that component would be easy to interpret. For instance, a component with high loadings on Na and Cl and low loadings on other variables could readily be interpreted as representing a rainwater / sea-salt influence in the samples. However, such a component may not necessarily be found as the *n* components in PCA are selected simply to be the simplest geometric projection of the overall data variability into *n* dimensions. Having derived provisional factors, generally (but not necessarily) by the Principal Components method, FA adds the step of clarifying the principal components (by "rotation" of the original component axes) with the aim of interpreting them in terms of real-world explanations. In the example above, the aim could be to maximise the chances that a factor represents rainwater influences only.

The method for rotation must be chosen carefully to ensure that false patterns are not introduced into the data by the rotation. The most common rotation method is the *varimax* rotation which rotates the components so as to maximise the variance within them. This ensures that each variable has the highest loading possible on a single component (e.g. Haag and Westrich, 2002): that is, loadings on each component for each variable are as close as possible either to ±1 or 0, with the subset of variables that is highly loaded having as little overlap as possible between components (e.g. Vega et al, 1998). It can be seen that this process will increase the likelihood of identifying underlying causes: in the example above Na and Cl are likely to be highly correlated and so all factor rotations will result in the loadings for these variables being similar, whilst the variance of the factor will be increased by setting the loading on the other variables to zero.

Choice of rotation is a subjective decision (Christophersen and Hooper, 1992) and there remains a danger of over-interpreting the data, effectively "choosing" a real world explanation *a priori* and then searching for a rotation that matches the hypothesis – that is, with FA there is a danger of allowing "the experimenter to impose his preconceived ideas on the raw data" (Blackith and Reyment, 1971), whereas principal components analysis is "simpler mathematically and...avoids some of the potential problems with 'factor indeterminacy' associated with factor analysis" (Stevens, 1996). This is particularly true if a rotation is chosen in which the factors do not remain orthogonal, and thus independent of each other – in PCA the components are always independent.

Furthermore the identification of factors, whether this is justifiable or not, is the central aim of FA and its use for other interpretive goals is more limited; conversely PCA can be conducted for several different motivations (section

3.4.1.2). For this reason rotation will not be used in this study and the analysis will be conducted as a PCA.

3.4.1.2 Details of the Principal Components Analysis method

PCA is a multivariate exploratory data analysis technique for use with datasets where the variables are "on an equal footing" (Chatfield and Collins, 1980): that is, there are generally not separate explanatory and response variables for each observation. The technique involves the transformation of a set of variables, some or all of which may be correlated, to a new set of uncorrelated components consisting of linear combinations of the original variables. There are three main motivations for this approach.

Firstly, the identification of the components may help to identify any underlying linear structure, trends or dimensions in a multivariate dataset – such trends may sometimes be referred to as "factors" but the technique should not be confused with Factor Analysis; an alternative term is "structural relationships" (Sprent, 1969). For example Haag and Westrich (2002) identified underlying controls on river water composition such as biological processes and discharge, from an original variable set consisting of numerous directly-measured water parameters such as conductivity, pH, and temperature (see description in section 3.4.3). The identification of explanatory trends in this way is accomplished primarily by observation of the grouping of variables into components, in the hope that variables that can be identified as being related to a common cause will be found to be strongly related to a common component. The fact that the principal components are uncorrelated helps ensure that each one is measuring a different dimension or trend in the data (Manly, 1986).

It can be argued (e.g. Chatfield and Collins, 1980) that such a process achieves little that could not be done by a direct analysis of the correlations between the variables, but equally the analysis of the components in this way can be taken further than implied by Chatfield and Collins (1980). For example one real-world source of trends or dimensions in the underlying data is where samples are taken representing mixtures formed from different combinations of end-members. In this case PCA can identify the trends in such a way as to point towards and even identify the mixing end-members, as demonstrated in an idealised example by Davies (2005) for a situation where the measured variables would be too numerous and too extensively correlated for such trends to be readily observed from the correlation matrix.

The second motivation for PCA is the reduction in the dimensionality of the data that can generally be achieved. Since each component may represent the variance from several variables and since the components are orthogonally rotated such that they are in decreasing order of the amount of variance explained, the first few components may represent most of the variance from the original data set, meaning that a larger proportion of the variance can be described by fewer variables than was possible with the original data set. Since the components are also orthogonal or uncorrelated, this is a useful technique prior to, for instance, multiple linear regression (as discussed in chapter 4), which can then be conducted on the components rather than the original variables.

The third motivation is related, namely as a variable reduction technique. Since components are ranked in order of the amount of variance in the original dataset that is explained, variables that do not correlate strongly to any component or only correlate strongly to components which explain little of the overall variance can be seen to contribute little information to the overall dataset. Once again this can be a useful technique prior to other analysis such as multiple linear regression, this time directly on the remaining original variables once those shown by the PCA to be irrelevant have been discarded.

The general technique of PCA was first suggested by Pearson (1901) and one of the first practical methods for computing the technique was proposed by Hotelling (1933). Principal components are calculated from the covariance matrix of the variables, generally after the variables are standardised to zero mean and unit variance – this is equivalent to saying that the components are calculated from the correlation matrix. If the variables are not standardised (principal components are calculated from the covariance matrix directly) then the variables are required to all be on the same scale to ensure equal weight in the analysis.

The eigenvalues of the correlation matrix **C** are equivalent to the variance of the principal components, and the coefficients of the principal components in terms of the standardised variables are given by the eigenvectors of **C.** These are selected and allocated to the PCs in an iterative process by finding at each stage the combination of coefficients such that the variance of the PC is maximised and (for all components except the first) such that the eigenvector is orthogonal to each of those already selected. This process is explained fully in Chatfield and Collins (1980). One key point to note is that there is an arbitrary choice of sign in the choice of the eigenvectors (due to the presence of square root terms in the matrix manipulation) and so the overall sign of each PC is also arbitrary. Additionally, if there are linearly dependent variables in the dataset (correlation = 1) then some eigenvalues will be zero; the number of linear constraints that can be found on the variables is equivalent to the number of zero eigenvalues.

Since the eigenvalues of the correlation matrix add to the sum of the diagonal terms (each of which is 1 in a correlation matrix), so too do the eigenvalues of the PCs; i.e. the total of the eigenvalues of the PCs is equivalent to the number of variables when analysis is conducted on the correlation matrix. This gives rise to a common algorithm for determining the number of PCs to retain in the analysis when the analysis is based on the correlation matrix: all PCs with an eigenvalue >1 plus the first PC with eigenvalue <1 – this is appropriate because PCs with an eigenvalue >1 are those which explain more variance than any one of the original variables could.

Although the concept of PCA is therefore simple – finding the eigenvalues and eigenvectors of the correlation or covariance matrix – the actual process of finding the eigenvectors subject to the constraints of orthogonality and maximising variance is computationally expensive and so the procedure did not become widespread until long after Hotelling (1933) proposed the key method. However this is no longer a problem and the method is implemented in most statistics packages; in this study the analyses were carried out in Minitab 14 and Stata 9.1.

3.4.2 PCA as a mixing analysis technique

PCA has been described above as being of use in identifying underlying structures in the dataset connecting causes of variability across several variables, allowing reduction of the dataset into a smaller number of components and interpreting these causes in terms of real world influences. It is a variable reduction technique, representing combinations of the input variables as a smaller number of underlying components or factors. This is of relevance to mixing analyses and hence to studies of catchment behaviour because conservatively-mixing waters that can be represented in terms of end members introduce precisely the kinds of patterns into the data collected from samples that PCA has been shown to be of use in identifying (e.g. Davies, 2005). Samples formed from various combinations of several end members, provided that those end members mix conservatively, will have compositions that can be described in terms of linear compositions of those end members. This is the key principle behind traditional end-member mixing analysis (EMMA) – once the compositions of the end members themselves are known. PCA can provide a method for achieving a similar result when the compositions of the end members are not known or, importantly, when measurements of sample compositions are not in terms of the same variables as the known end member compositions (for example, Davies (2005), where the measured variables are sample absorbances at various wavelengths and the mixing / end members were in terms of concentrations of three chemicals).

The basic method is to plot PC scores for one component against another and to examine the distribution of those scores; often these will form a clearly-identifiable pattern or shape with end members at vertices as in the idealised example given by Davies (2005). The principal components themselves do not (necessarily) identify end members; that is, the end members will not necessarily lie on the axes of the PC plot. Rather, each principal component is assumed to represent a process or pattern in the mixing of the end members, and plotting scores of the principal components against one another will then reveal the end member data points.

3.4.3 Previous studies

A wide range of previous studies have shown the utility of PCA and FA for identifying trends in multivariate datasets collected from water samples across a catchment over a range of times, and to a lesser extent, locations. The majority of these have been concerned chiefly with interpreting the results in terms of underlying mechanisms or factors, whilst a smaller number have conducted more detailed analysis of the trends between the identified components, rather than the loadings of the components *per se*, in order to make inferences about mixing sources or other catchment behaviour.

Haag and Westrich (2002) studied the River Neckar in Germany, collecting samples from each of six sites along the main river over a five-year period and analysing these for ten water quality variables: Chlorophyll-a, Biological Oxygen Demand, Conductivity, pH, water temperature, ammonium, nitrite, nitrate, phosphate, and dissolved oxygen. Samples were collected every two weeks for the five years and the study was therefore primarily concerned with temporal variations. After PCA on the entire dataset a varimax rotation was used, giving a FA procedure. Four components were retained. The loadings on these components were such that Haag and Westrich (2002) were able to interpret each component as representing a different set of influences on the water quality, according to which variables had high loadings on each component, and knowledge of what natural processes influence each variable. The first component had high loadings on chlorophyll concentration, phosphate concentration, oxygen saturation and pH and was interpreted as representing biological influences, because the high chlorophyll concentration, high oxygen saturation, and raised pH (due to the consumption of CO_2) were indicative of photosynthesis. The second component had high loadings on discharge rate, conductivity, nitrate, and phosphate concentrations and was interpreted as representing variations linked to discharge (for instance conductivity decreased with greater dilution under high flow conditions). The third component was interpreted as representing seasonal influences on water quality, with high loadings on water temperature and chlorophyll concentration, and somewhat lower loadings on ammonium and nitrate. The fourth component was identified as a wastewater influence, with high loadings on biological oxygen demand, ammonium, and nitrite.

Haag and Westrich (2002) confirmed their interpretation of the biological and wastewater components by removing from the data the effect of the "external forcing" of water temperature and discharge (the study was concerned with in-river processes; temperature and discharge are not governed by these and therefore could affect the results) and then repeating the analysis. Aside from removing the discharge and seasonal components described above, this did not significantly affect the loadings on the "biological" and "wastewater" components which were therefore deemed to be independent of seasonal and discharge variations. Furthermore, Haag and Westrich (2002) analysed the data for each of the six sampling sites separately, and generally similar results were found for each site indicating that the same processes were applicable throughout the river system. The study of Haag and Westrich (2002) therefore demonstrated how extraction of principal components can be combined with knowledge of likely processes or interactions to identify underlying causes behind observed water quality variations, by observation of the loadings on each component.

Petersen et al (2001) analysed samples collected fortnightly over a five year period from 14 sites on the River Elbe in Germany. The samples were once again analysed primarily for nutrients rather than inorganic solutes, and as with Haag and Westrich (2002) the study was therefore concerned chiefly with identifying underlying organic and biological controls on the water quality rather than geological or geographical controls such as rock type. Petersen et al (2001) introduced a LOWESS smoothing method for the elimination of external forcing caused by discharge and temperature; the method was later used by Haag and Westrich (2002). Once again Petersen et al (2001), whilst concerned primarily with organic influences, demonstrated the utility of PCA as a technique for identifying underlying influences from a diverse set of water quality variables. Petersen et al (2001) also applied the bootstrap method (eg Efron ,1986) in the estimation of the component loadings enabling the generation of "pseudo" confidence intervals for the variable loading estimates – this procedure is very similar to the jack-knife procedure of Martens and Martens (2000) that is used in chapter 4 of this study for derivation of confidence intervals for PLS regression coefficients.

Evans et al (1996) studied four streams in the Adirondack Mountains over a 2-year period. As with the above two studies, this was primarily concerned with temporal rather than spatial variation but samples were analysed for a wider range of inorganic solutes, allowing the application of results to the identification of water sources as well as in-stream processes. This study was prior to the introduction by Petersen et al (2001) of LOWESS smoothing as a method to eliminate seasonal external forcing; Evans et al (1996) subdivided the data into 2-monthly sections to reduce seasonal (but not discharge) forcing whilst still having data groups large enough for reliable analysis.

The studies described above illustrate the use of PCA for identifying underlying factors behind the observed composition of river waters. However they pertain primarily to the results of processes operating within the river itself. Christophersen and Hooper (1992) discuss the use of PCA specifically for analysis of mixing of source waters and compare the technique to the more classical end-member mixing analysis (EMMA). The authors state that EMMA is appropriate if source waters are available that are indeed extreme enough to be considered *a priori* as "end members" – for instance soil water and precipitation – and if their combination is known, in which case a least-squares method is used to identify the combination of source waters present in each stream sample. Mathematically the technique is similar in concept to solving simultaneous equations. This approach is known as a "forward analysis" (Christophersen and Hooper, 1992). PCA provides the reverse approach, attempting to identify from the samples the number and composition of the source water end members. The components do not necessarily represent end members themselves but rather underlying patterns in the data, which can be combined to represent end members. Christophersen and Hooper (1992) give the example of a component loading strongly on hydrogen ions, sulphate and nitrate representing an acid component; this does not mean that a given dataset will necessarily contain samples with large scores only on this component, but rather that there may be samples scoring positively on this component and negatively on another component. That is, the end members do not necessarily lie on the axes of the space defined by the components, but when the scores of various components are plotted against one another the end members can be observed as circumscribing the data.

Christophersen and Hooper (1992) argue that this PCA approach cannot unambiguously identify the source water compositions and is therefore not always appropriate in stream sampling, because a given dataset does not necessarily include samples of each of the end members. The PCA analysis cannot identify end members that lie outside the space sampled. However the authors accept that PCA is nonetheless useful in determining the *number* of end members (source waters) and in suggesting potential compositions. These proposed end member compositions can then be analysed by a forward EMMA technique to determine how well they can predict the observed stream compositions, and therefore to judge how appropriate the results of the PCA are.

Vogt and Muniz (1997) studied variations in the water chemistry from the outlet of a small (18.7ha) catchment at Ingerbakken, Norway. The catchment was largely peat-covered, above a mineral gley layer and gneiss bedrock. In parts of the catchment there was little or no drift cover and the bedrock was exposed. Christophersen et al (1990) had studied this same catchment and used EMMA to identify flowpaths, concluding that baseflow was supported primarily from the mineral gley soils underlying the peat, with quickflow discharge originating from the peat layers. Vogt and Muniz (1997) took this two end member composition (groundwater baseflow originating from mineral soils, and near-surface quickflow originating from humic acidic soils) as a starting point for their analysis. They studied samples taken over a period of just under two years, collected at irregular intervals from the catchment outlet and also from several soil-water lysimeters. Soil samples were also analysed. Samples were variously analysed for H, Na, Ca, Mg, ammonium, nitrate, sulphate, chloride, bicarbonate, TOC, TIC, monomeric and complexed Al, and acid buffering capability (not all samples were analysed for all of these constituents). The data were firstly analysed in terms of a general conceptual analysis of the variations in water chemistry over time and the relationships between the different solutes, in order to establish the change in water sources with flow conditions. Secondly PCA was used to further examine the relationships between solute variations and place these in context of changes in water source and flow pathways. Through the identification of a discharge-dominated component, the effect of discharge variations on concentrations could be accounted for and therefore those variations in chemistry due to flowpath changes could be identified. This enabled the authors to conclude that even during quickflow periods, when the flow is heavily dominated by near-surface waters, and in an apparently impermeable catchment, the mineral lower layers of the catchment nonetheless contribute a significant influence to the water chemistry (Vogt and Muniz 1997). This also corresponds to the finding of Neal et al (1986) from upland catchments in North Wales. In the context of peat catchments such as many of those in the present study, this finding indicates that flow through the mineral layers underlying the peat represents an important flowpath, in addition to the flowpath through surface peat layers, under a wide range of flow conditions and not just under baseflow conditions.

Worrall et al (2003b) demonstrated the use of PCA for mixing analysis and the identification of end members in upland areas, applying the technique to samples collected from a range of sites and subcatchments across the 11.4km^2 Trout Beck catchment described in chapter 2. Sites included a range of streams in addition to soil waters and precipitation. Samples were analysed for a range of metals, nitrogen, sulphate, and other natural parameters. The study identified five key principal components, representing respectively overall concentration; Fe, Al, and colour; K; N and Na; K and Cl. Analysis in this study was largely in terms of the trends in samples indicated by the principal components, used to trace the source and evolution of sample waters, rather than in terms of identifying underlying processes or factors as in some other studies such as Haag and Westrich (2002) and Petersen et al (2001). Having run a single PCA on the bulk data of all samples and solutes collected for the study, Worrall et al (2003b) conducted an extensive analysis of the results of the PCA to assess not only mixing of the waters, but also the evolution of the waters from the source end members. This was achieved by comparing samples along potential flow paths from precipitation and ground water, through soil water, to streamflow. For example, the study assessed the evolution in chemistry of soil waters over time and compared this to the chemistry of the precipitation, leading to the conclusion that soil water was well buffered against changes in precipitation chemistry (Worrall et al 2003b). A similar process was applied to compare soil waters and the associated first-order streams. These aspects of the study illustrate the use of PCA to assess the effect of an input water on a system: a principle that could equally be extended to the study of nested catchments such as many of those in the present study.

Whilst Christopherson and Hooper (1992) represented as a problem the fact that PCA cannot identify *end members* falling outside the *sample* space – i.e. for each end member at least one sample must consist 100% of that end-member – Worrall et al (2003b) approach the same fact from an alternative viewpoint, favouring PCA because EMMA as a simple algebraic combination of end members cannot handle *samples* that fall outside the *end-member* space. That is, if the end-members are not known and determined correctly, then the analysis fails as there is no way of representing a composition more extreme than one of the sampled end-members. This statement may seem intuitive but in the context of this study it is relevant because groundwaters will not be directly sampled at the grip sites, meaning that if one site is taken to represent a groundwater end member, any subsequently identified sites that are even closer to groundwater in character could not be represented. The problem raised by Christophersen and Hooper (1992) is effectively that PCA cannot identify the actual composition of any end members not sampled. However, Worrall et al (2003b) show that even if the precise composition of such end members cannot be determined this does not mean their actual existence cannot be inferred, since analysis of the trends in the data as revealed through the principal components may nonetheless suggest the presence of such end members. In particular, Worrall et al (2003b) demonstrated the advantage of PCA in this situation by inferring a ground water end member that contributed to the samples observed. Although this end member was not sampled and possibly fell outside the sampled space, its presence could rather be inferred from the evolution trend of the water from this unsampled end member into the range of the sampled space.

3.4.4 Data description

During the sampling campaigns described in chapter 2 and section 3.2 to monitor DOC export from the grip sites at Hexhamshire Common and Cowgreen, regular site visits were made to collect the automatic samples. On these visits, manual grab samples were also collected using pre-rinsed wide-mouthed 1l Nalgene sample bottles. These samples were taken where there was sufficient water in the grips to immerse the sample bottle, and where weather conditions permitted.

On return to the laboratory, the samples were stored frozen prior to analysis for base metal cations using a Perkin Elmer ICP-OES machine. Analysis was conducted on acidified unfiltered samples and instrument drift or autosampler problems were detected and corrected using a 1 mg l^{-1} Y spike (see chapter 5 for details of the analysis protocol). Samples were analysed for Al, Ca, Fe, K, Mg, Na and Si.

In order to compare the grip waters with raw rain and soil waters, data were obtained from the ECN monitoring programme at Moor House. In addition to the precipitation chemistry data described in section 3.2, data for shallow soil water and deep soil water samples were also obtained. The samples were collected at depths of 10cm and 50cm respectively using suction samplers, from the catchment of the Cottage Hill Sike first order stream in the Moor House NNR. The samples were analysed for base metal cations including Al, Ca, Fe, K, Mg and Na by the ECN monitoring programme. Concentration of Si was not available for the ECN samples and so the Si data have been excluded from the analyses in this chapter. The sampling regime, date range, and the total number of samples analysed from each site are shown in Table 3.2. Data from the soil water samples at Moor House were not obtained for the full period that was covered by the grip samples; however these data were used in the following analyses only to identify end member behaviour rather than to identify trends across a period of time.

Site	Number of samples	Approx frequency	Date range
Hexham 1	31	Opportunistic on site visits: weekly – monthly	October 2002 – November 2004
Hexham 2	60	Opportunistic on site visits: weekly – fortnightly	October 2002 – December 2004
Hexham 3	57	Opportunistic on site visits: weekly – monthly	October 2002 – December 2004
Cowgreen	53	Opportunistic on site visits: weekly - monthly	October 2002 – February 2005
Rain	106	Weekly from ECN programme	October 2002 – December 2005
Shallow soil water	27	Fortnightly – monthly from ECN programme	April 2004 – June 2005
Deep soil water	19	Fortnightly from ECN programme	April 2005 – December 2005

Table 3.2 Description of sample collections from each site

3.4.5 Solute concentration results

Concentrations of each metal are shown by source in Figure 3.22. Box-whisker plot definitions are as given in section 3.3.1. Two outlier points in the imported Moorhouse rain dataset were excluded which had Al concentrations in excess of two orders of magnitude higher than any other samples whilst concentrations were not higher in any of the other elements. All solutes were significantly correlated with one another ($P<0.05$) with the exception of K vs. Ca and K vs. Fe (Table 3.3).

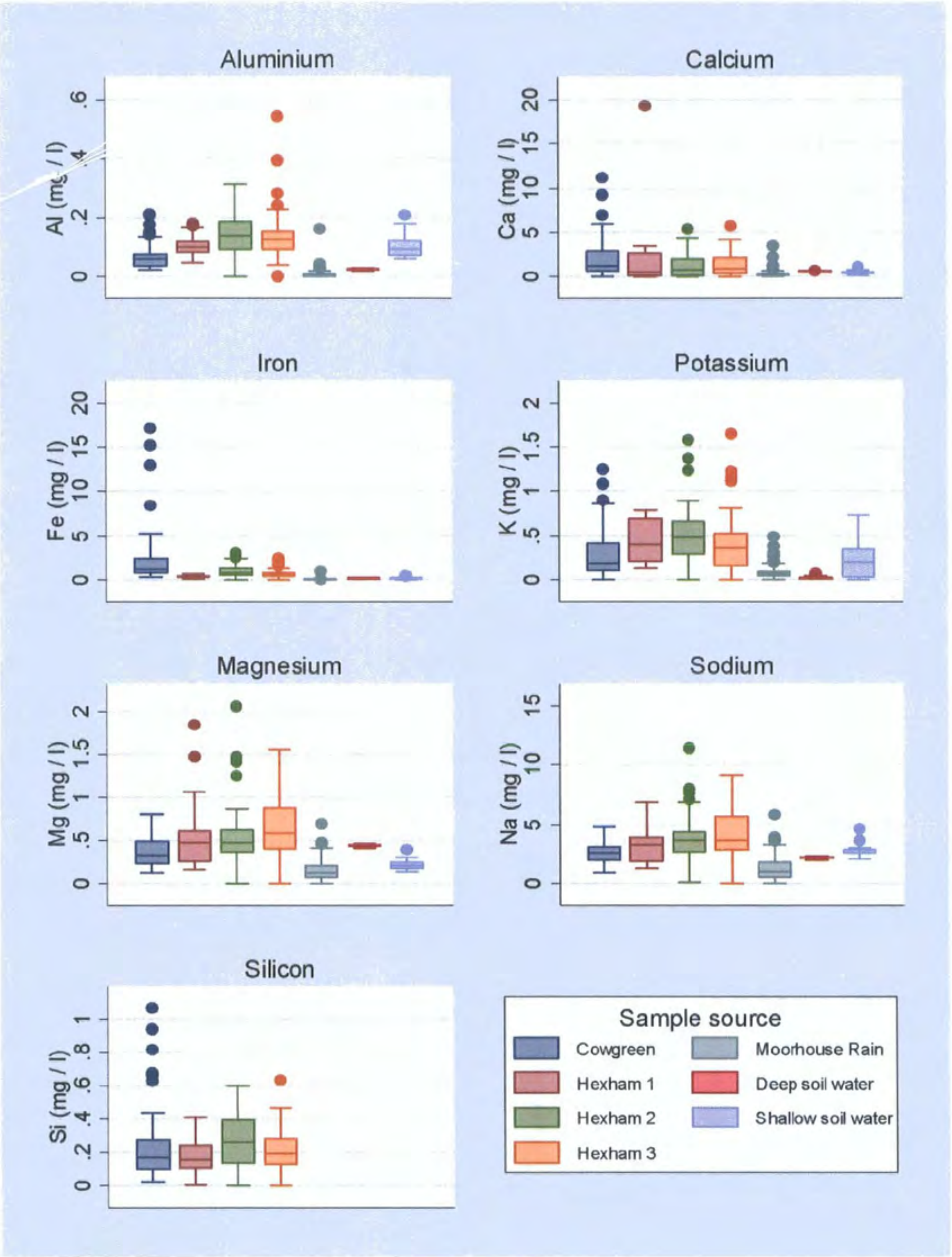


Figure 3.22 Box-whisker plots showing solute concentrations in the samples entered into the first PCA

	Al	Ca	Fe	K	Mg	Na
Al	1					
Ca	**0.3902**	1				
Fe	**0.386**	**0.3177**	1			
K	**0.3466**	-0.0582	0.0211	1		
Mg	**0.6029**	**0.2449**	**0.2167**	**0.2601**	1	
Na	**0.6465**	**0.2575**	**0.1821**	**0.3113**	**0.8862**	1

Table 3.3 Correlation matrix for the variables entered into the PCA. Shaded cells indicate correlations significant at P<0.05.

3.4.6 PCA: loadings and scores

A Principal Components Analysis was conducted on the six solutes for which each site had data. All variables were on the same scale (mg l^{-1}) but since the range of values varied over at least two orders of magnitude, the analysis was run using the correlation matrix. The number of components to retain was determined by including all those with an eigenvalue > 1 and the first component with an eigenvalue < 1 (Table 3.4); the scree test was also applied for visual selection of components (Figure 3.23). Both methods suggested the retention of three components; the loading plots for these are shown in figure Figure 3.24 and Figure 3.25.

Component 1 has strong loadings of equal sign (positive) on all the variables. The first component is often found in PCA to represent some measure of overall concentration or size (as appropriate to the data), e.g. Worrall et al (2003b); Manly (1986). This does appear to be the case in this analysis, and the component scores are as would be expected (e.g. Figure 3.27) with rainwater samples forming a low end member with respect to PC1 and all other samples, having had contact with soil, scoring higher. The large eigenvalue of component 1 and the high proportion of variance (47.8%) that it explains suggest that by far the greatest difference between samples is in terms of the overall concentration, as opposed to differences such as between site behaviours which could lead to varying solute ratios. This is in agreement with the similar pH / conductivity relationships observed for each site in section 3.2

and the observations in section 3.3.1 regarding differences in concentration between Hexham 2 and Hexham 3, and can partially be explained in light of the inclusion of both fresh rainwater samples and evolved grip and soil water samples meaning that large concentration differences within the dataset are to be expected. Additionally the dataset includes grip samples from across the range of flow conditions, including ponded water whose concentration would increase through evaporation.

Component 2 distinguishes primarily between Ca and Fe (strong positive loadings) and K (strong negative loading). Component 3 has strong positive loading on Fe and K, and somewhat smaller negative loadings on Mg and Na. These results are somewhat harder to interpret: a component that distinguishes peat soil water from other waters would distinguish Al and Fe from the other variables as these are the metals whose solubility is most affected by increasing acidity; such a contrast is found in the PCA described in chapter 5 but is not observed here. Component 2 clearly represents the lack of correlation between Ca and Fe vs. K, but the reasons for this are unclear. The solute that is strongest in rainwater is Na; it could be suggested that component 3 points to cation exchange processes that differ between sites, with Na exchanging for Ca in some cases and for K in other cases. This does suggest that component 3 is the component most likely to distinguish between the sites, but from these data it is difficult to draw firm conclusions about the reasons behind such an interpretation.

Variable	1	2	3	4	5	6
Al	0.5047	0.04543	0.1495	0.07503	-0.84167	0.08264
Ca	0.28162	0.58279	-0.11275	0.71286	0.245	0.01169
Fe	0.26499	0.54019	0.53948	-0.53929	0.23043	-0.05483
K	0.24593	-0.54182	0.66615	0.35746	0.27126	0.02898
Mg	0.51205	-0.17337	-0.35354	-0.2241	0.28104	0.67346
Na	0.52256	-0.20702	-0.32427	-0.13181	0.16096	-0.73187
Eigenvalue	2.87035	1.21472	0.81515	0.64692	0.34408	0.10877
Difference	1.65563	0.39957	0.16823	0.30284	0.23531	.
Proportion	0.4784	0.2025	0.1359	0.1078	0.0573	0.0181
Cumulative	0.4784	0.6808	0.8167	0.9245	0.9819	1

Table 3.4 Results of the PCA on all samples

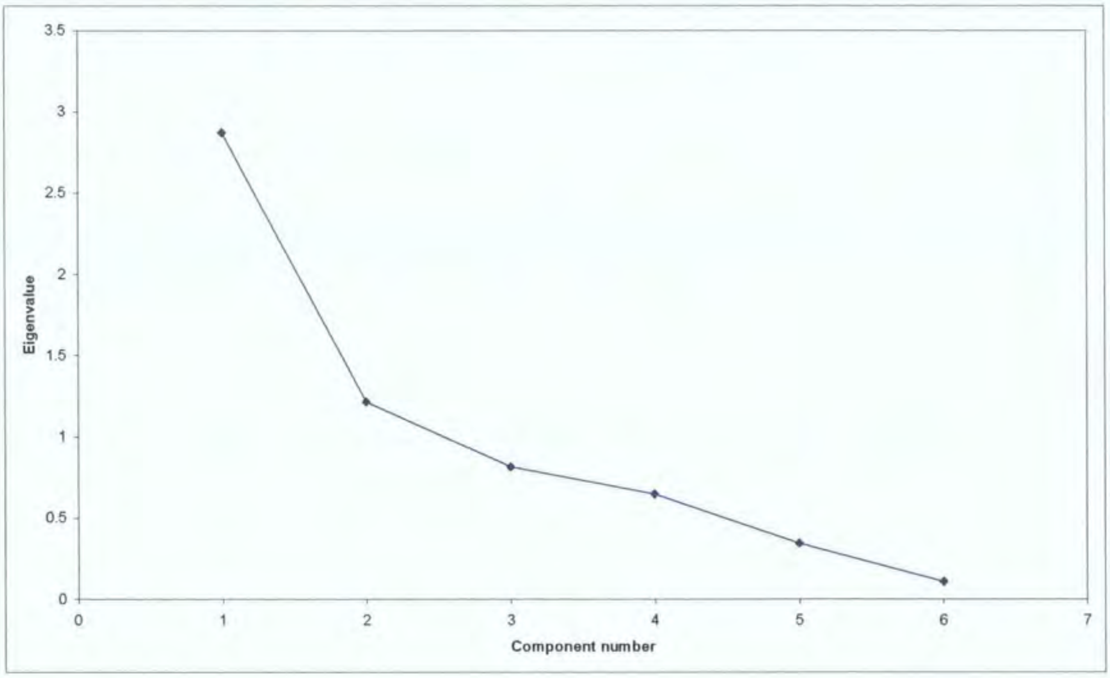


Figure 3.23 Scree plot of the eigenvalues for the first PCA analysis

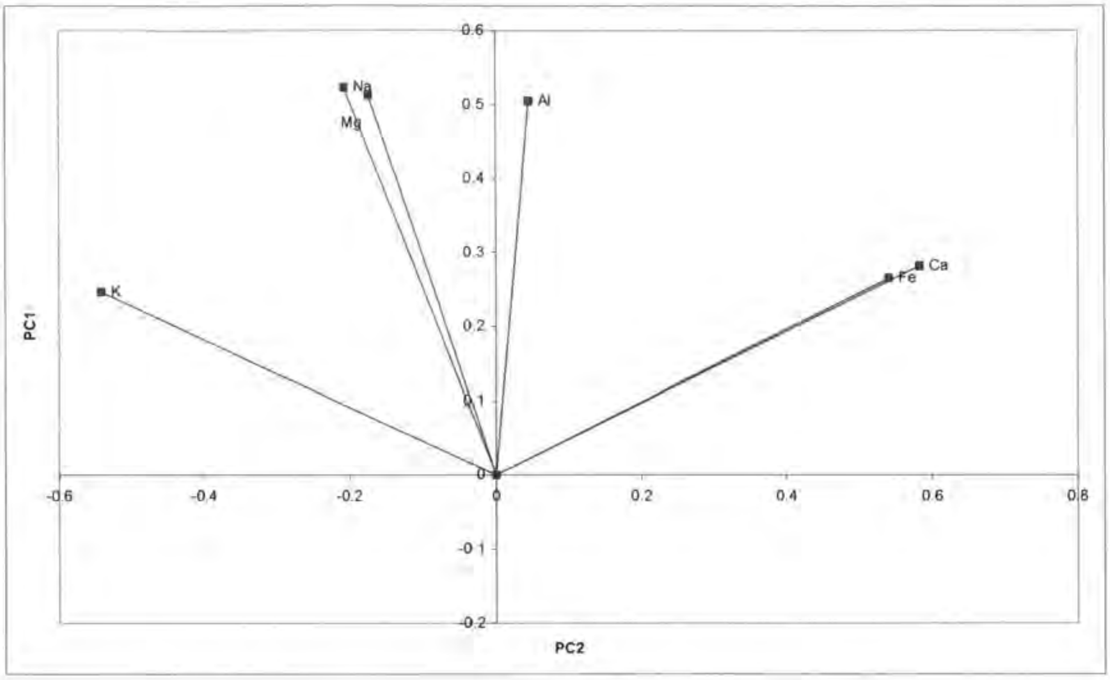


Figure 3.24 Loading plot of PC1/PC2 for the first analysis

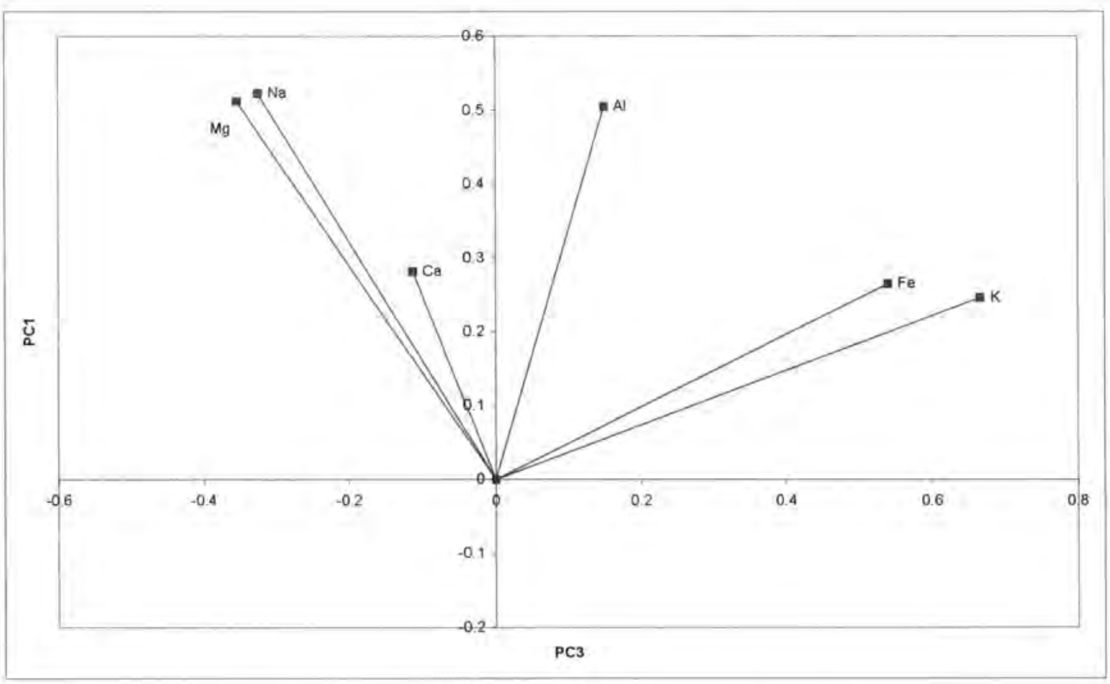


Figure 3.25 Loading plot of PC1/PC3 for the first analysis

The first three PCs were scored for each sample and are plotted against one another in Figure 3.26 and Figure 3.27, separated by site. From Figure 3.26 it is clear that the greatest contrast on PC2 is to separate some Cowgreen samples (and one from Hexham 1) from the remainder by higher PC2 scores.

The outlying Cowgreen samples are from dry periods, chiefly Summer 2003, whilst the outlying Hexham 1 sample is from a major storm on 11/08/2004. No other specific groupings are observed relative to PC2 with the exception of deep soil water samples with all score in a tightly constrained region relative to both PC1 and PC2, at the lower end of the range of PC1 scores and in the middle of PC2 scores. Rainwater samples almost all score low on PC1 due to low overall concentration.

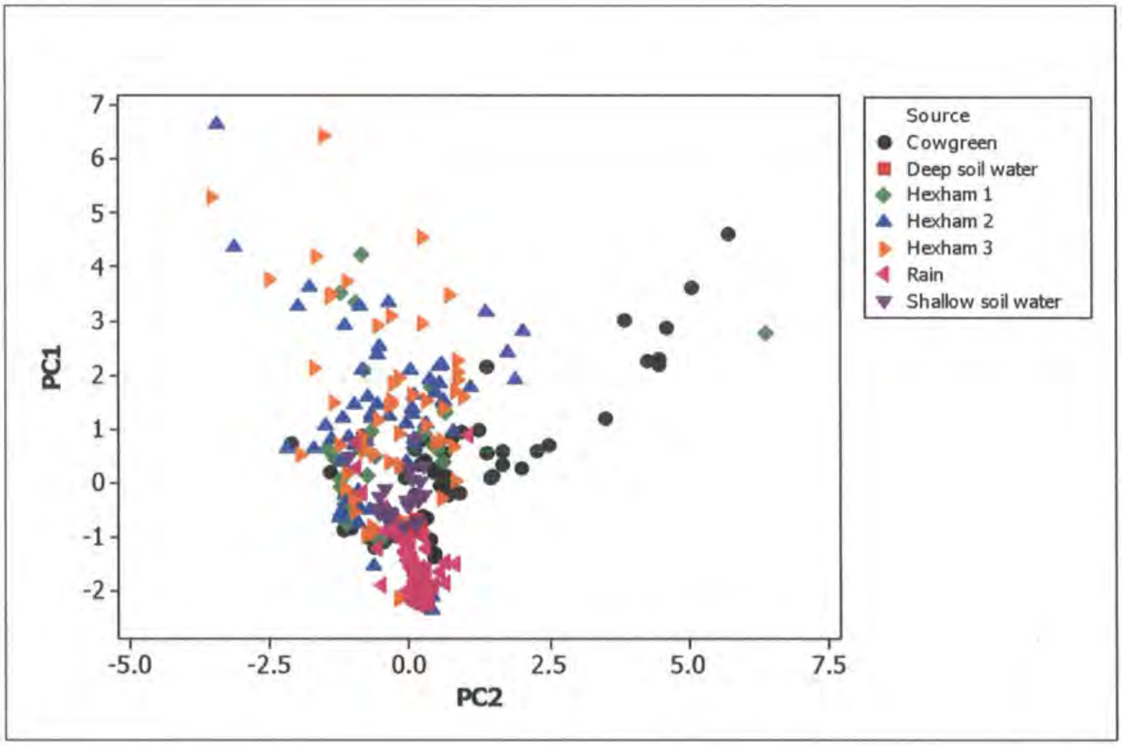


Figure 3.26 Score plot of PC1/PC2 for the first analysis, for all samples grouped by site

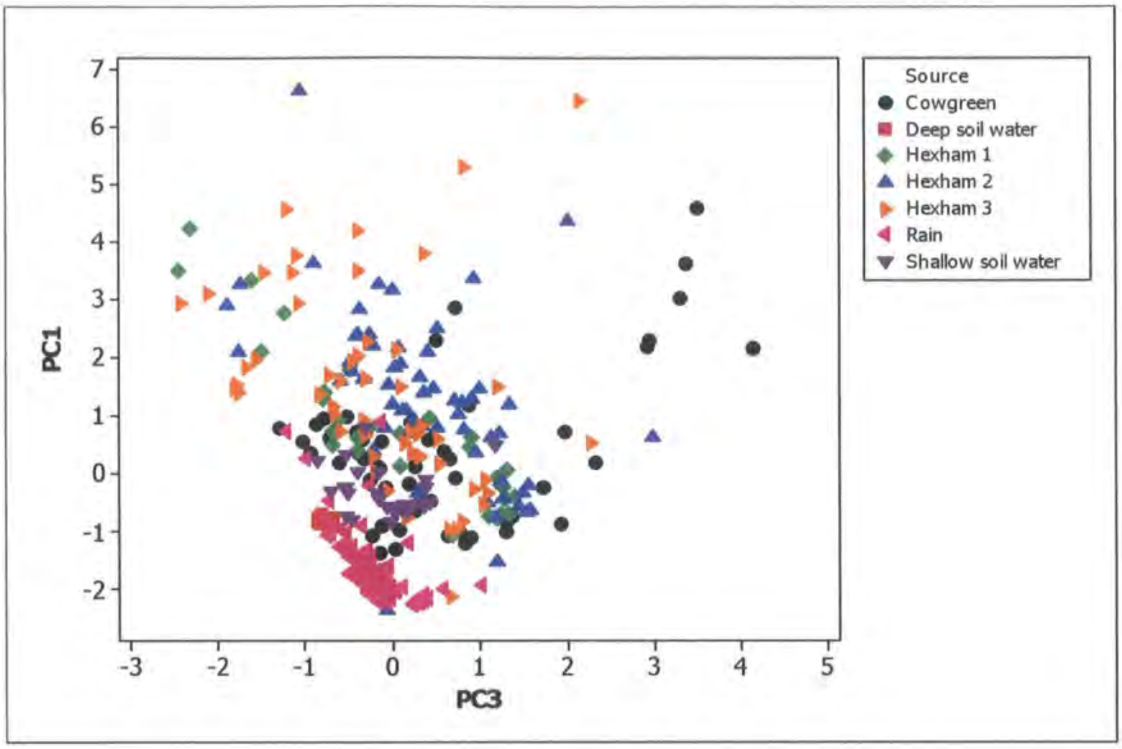


Figure 3.27 Score plot of PC1/PC3 for the first analysis, for all samples grouped by site

From the plot of PC1 against PC3 a number of trends can be suggested. Rainwater samples lie along two key trends, firstly of increasing negative PC3 vs. increasing positive PC1, and secondly of increasing positive PC3 vs. little change in PC1. Of these, the majority of samples lie along the first trend. Deep soil waters are all constrained to the highest PC1 end of the first rainwater trend: the composition of the deep soil samples is relatively invariant (Figure 3.27). This implies that deep soil water is chemically little-altered from rainwater, indicative of the relatively inert nature of the catotelm.

The scores for the remaining sites appear to be bounded by two trends, largely similar to the rainwater trends, away from the most negative-PC1 rainwater samples: i.e. firstly in the direction of increasing negative PC3 vs. increasing positive PC1, and secondly in the direction of increasing positive PC3 vs. increasing positive PC1. However although these trends appear to be clear there are no samples that can be identified as end-members to either trend, in order to develop an end-member mixing model.

Finally there is some indication that the behaviour of the grip sites may change systematically in trends that parallel the first rainwater trend described above.

This is most visually obvious in Figure 3.27 for the samples from the three Hexham sites, with the samples from each site appearing to lie on a trend that is sub-parallel to the first rainwater trend, with the Hexham 2 samples being at a greater distance from the rainwater trend than the Hexham 3 samples and the Hexham 1 samples being closer to the rainwater trend than either of these. Fitting a best-fit least squares regression line to the data for each site confirms this observation for Hexham 1 and Hexham 2, whilst the gradient (change in PC1) is somewhat less for the Hexham 3 samples (Figure 3.28)

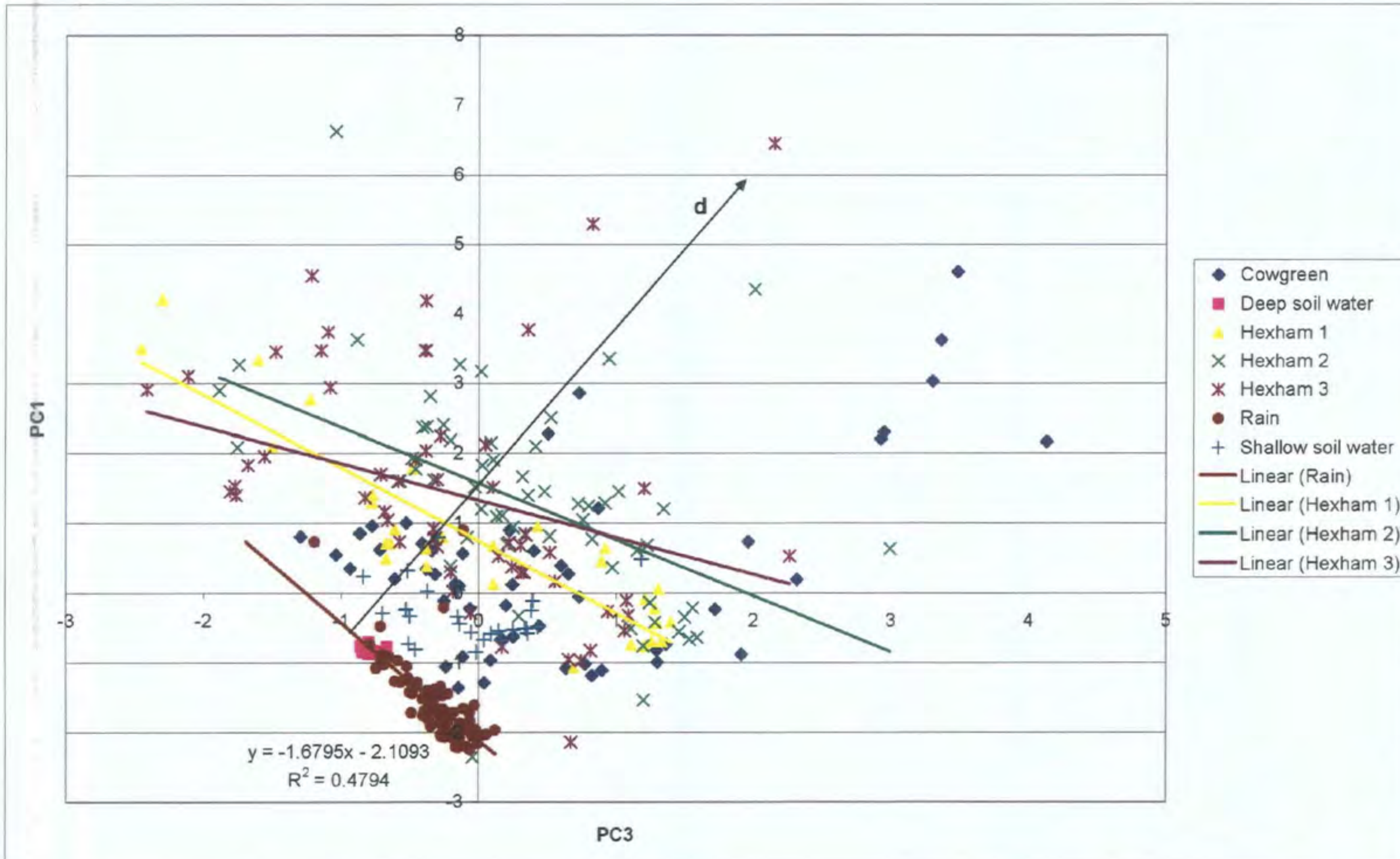


Figure 3.28 Score plot of PC1/PC3 for the first analysis, showing best-fit lines for rain and Hexham sites, and line orthogonal to main rainwater trend.
Only rainwater samples on the main trend are shown. Details of fit are shown for main rainwater trend.

3.4.7 PCA: ANOVA of results and discussion

The PCA described in 3.4.6 was used in order to test the hypothesis that there are differences between the sites that can be observed in terms of the solute chemistry. The samples were analysed in terms of the trends observed in the previous section for the PC1 vs. PC3 plot. These trends were observed visually, backed up by fitting best-fit least squares regression lines to the graphs (Figure 3.28). An alternative is an end-member mixing analysis based on the score plots (as described in section 3.4.2); however in this case there were no clear end-member samples observed in the score plots so an end-member mixing analysis could not be conducted.

In order to test the significance of the differences between the trends for rainwater and the individual grips, the distance of each point orthogonal to the main rainwater trend was calculated (that is, the distance of each point from the rainwater trend indicated in red, in the direction indicated by line *d*, Figure 3.28). The best-fit equation representing the main rainwater trend (those rainwater samples with a PC3 score < 0.2, Figure 3.27) was PC1 = -2.109 - 1.680*PC3. Trigonometrically this gives the angle of the trend, expressed as rotation anticlockwise from the y-axis, as 38.5° (note that the differing y and x scales in Figure 3.28 mean that this is not the angle shown in the figure as printed). For each sample falling to the right of this trend the distance *d* was calculated as the perpendicular distance from this trend.

In order to test for differences between sites a two way ANOVA procedure was conducted, using sampling site and sampling date as the fixed factors and using distance *d* and the score on PC1, PC2 and PC3 as response variables.

ANOVA tests against the null hypothesis that the means of several populations, defined by levels of one or more factors, are equal. This is achieved by comparison of the variance of the means of each factor level with that of the population mean, allowing the null hypothesis (that the factor does not have an influence and the means are equal) to be either accepted or rejected with a given confidence level.

Where there are several levels of a factor, each factor level must be compared to each other level in order to determine if there is a difference between any of the levels: in this case, each site must be compared to each other site. Making multiple comparisons in this way increases the probability of making a type I error (in this example, concluding that there is a difference between sites when in fact none exists). For example, if comparisons are made at a confidence interval of $P<0.95$, then the probability of making the correct decision on one test is 0.95. However, if there are three groups to compare, then there are three pairwise comparisons between groups (Groups 1 vs. 2; Groups 1 vs. 3; Groups 2 vs. 3). The probability of avoiding any Type I error is then decreased: $0.95*0.95*0.95 = 0.86$.

This problem is addressed through the use of the Tukey post-hoc method to test for significant differences between the sites for each ANOVA. This method determines the required confidence interval for each individual pairwise comparison in order to maintain the desired confidence for the overall set of pairwise comparisons.

Since not all sites were sampled on each date, the data were unbalanced, and therefore the effect of the interaction between the factors – the variation of each site with time – could not be calculated. Therefore for each end-member the ANOVA procedure was conducted twice: firstly as a two-way procedure with site and date as separate fixed factors but without analysis of the interaction between these terms, and secondly as a one-way ANOVA with site as the only factor. Date was analysed as an unscaled (categorical) variable so the presence or absence of variation with time could be identified, but could not be quantified as a seasonal, flow-dependent or other effect.

Selection of appropriate tests for the magnitude of significant effects in ANOVA was with reference to the summary given by Halderson and Glasnapp (1972). The η^2 values are calculated as SS_{factor} / SS_{total} and therefore represent the percentage of the total variance in the dependent variable that is accounted for by each factor – this is analagous to R^2 in regression analysis. Because the SS_{total} for a model varies if more factors are added but the SS_{factor} does not, so the η^2 value varies and is not an appropriate measure when the number of factors is varied. This means that in most cases, where not every possible factor that could affect the dependent variable is modelled, η^2 cannot be taken to be indicative of the degree of variance explained by that factor in the overall population (Halderson and Glasnapp, 1972). Hays (1963) introduced the ω^2 statistic in an attempt to address this problem. This estimates the proportion of the total population variance that is explained by each factor, by taking into account the expected mean squares values for the population. ω^2 values are calculated using the formula in Equation 3.1 and a result of over 0.15 is deemed a "large" effect; 0.06 – 0.15 is a "medium" effect, less than 0.06 is a "small" effect (Cohen, 1977).

$$\omega^2 = \frac{SS_{factor} - DF_{factor} * MS_{error}}{SS_{total} + MS_{error}}$$

Equation 3.1 Calculation of ω^2. DF = degrees of freedom: the number of categories - 1

Results from the ANOVA and significance tests for each principal component and the orthogonal distance from the rainwater trend, d, are shown in Table 3.5 – Table 3.14. All P-values in the ANOVA tables represent the probability that the factor does not have an influence on the relevant response variable; all P-values in the post-hoc significance test tables represent the probability that no difference exists between the sites. To aid interpretation, results significant with $P < 0.05$ are shaded in blue, differences of significance $0.05 < P < 0.10$ are shaded in yellow, and differences of significance $0.10 < P < 0.20$ are shaded in pink. As the effect of site was highly significant for all variables, all Tukey post-hoc tests were performed (these should not be performed if the effect of a factor is not significant).

Two-factor	PC1			PC2			PC3			d		
	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2
Site	0.00	0.58	0.57	0.00	0.10	0.08	0.00	0.23	0.21	0.00	0.56	0.55
Date	0.17	0.27	0.04	0.23	0.56	0.07	0.11	0.50	0.10	0.01	0.25	0.07
Error		0.15			0.34			0.27			0.19	

Table 3.5 ANOVA table for two factor analysis on PC1 – PC3 and d

PC1 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.52					
Hexham 2	0.09	>0.995				
Hexham 3	0.29	>0.995	>0.995			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	0.90	0.21	0.06	0.13	0.09	
Shallow	0.99	0.30	0.06	0.16	<0.00	0.99

Table 3.6 Post-hoc significance tests between sample sources, response variable PC1

PC2 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.76					
Hexham 2	0.01	0.48				
Hexham 3	0.09	0.91	0.97			
Rain	0.92	>0.995	0.35	0.83		
Deep	0.92	>0.995	0.92	>0.995	>0.995	
Shallow	0.01	0.26	0.97	0.71	0.01	0.34

Table 3.7 Post-hoc significance tests between sample sources, response variable PC2

PC3 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.16					
Hexham 2	0.38	0.99				
Hexham 3	<0.005	0.33	0.04			
Rain	<0.005	0.60	0.13	>0.995		
Deep	<0.005	0.01	<0.005	0.17	0.02	
Shallow	0.02	0.89	0.44	>0.995	>0.995	0.02

Table 3.8 Post-hoc significance tests between sample sources, response variable PC3

d 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.99					
Hexham 2	0.53	0.94				
Hexham 3	>0.995	>0.995	0.39			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	<0.005	<0.005	<0.005	<0.005	>0.995	
Shallow	0.48	0.38	0.05	0.52	<0.005	0.04

Table 3.9 Post-hoc significance tests between sample sources, response variable d

One factor	PC1			PC2			PC3			d		
	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2
Site	0.00	0.58	0.56	0.00	0.10	0.08	0.00	0.23	0.21	0.00	0.56	0.55
Error		0.42			0.90			0.77			0.44	

Table 3.10 ANOVA table for one-factor analysis on PC1 – PC3 and d

PC1 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.94					
Hexham 2	<0.005	0.18				
Hexham 3	0.29	0.96	0.71			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	0.03	<0.005	<0.005	<0.005	<0.005	
Shallow	0.57	0.09	<0.005	<0.005	<0.005	0.73

Table 3.11 Post-hoc significance tests between sample sources, response variable PC1

PC2 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.02					
Hexham 2	0.03	>0.995				
Hexham 3	0.02	>0.995	>0.995			
Rain	0.86	0.06	0.11	0.05		
Deep	0.98	0.24	0.39	0.26	>0.995	
Shallow	0.08	0.99	>0.995	>0.995	0.26	0.58

Table 3.12 Post-hoc significance tests between sample sources, response variable PC2

PC3 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.36					
Hexham 2	0.80	0.98				
Hexham 3	<0.005	0.16	0.01			
Rain	<0.005	0.27	<0.005	0.98		
Deep	<0.005	<0.005	<0.005	0.11	<0.005	
Shallow	<0.005	0.75	0.14	0.92	>0.995	<0.005

Table 3.13 Post-hoc significance tests between sample sources, response variable PC3

d 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.92					
Hexham 2	0.50	0.09				
Hexham 3	>0.995	0.87	0.57			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	<0.005	<0.005	<0.005	<0.005	>0.995	
Shallow	<0.005	0.02	<0.005	<0.005	<0.005	0.01

Table 3.14 Post-hoc significance tests between sample sources, response variable d

3.4.7.1 PC1

Principal component 1 (PC1) is primarily a measure of sample concentration (section 3.4.6). Differences between sites explained 58% of the overall variation in this component, and the ω^2 of 0.57 represents a very large effect. However these differences cannot be attributed to differences between the grips, with none of the grips being significantly different from one another at $P<0.05$ and only Hexham 2 and Cowgreen being possibly different at $P<0.10$. The large proportion of the variation of this component that is explained by site is therefore likely to be attributable to the difference in concentration between source (rain) water and the other sites; all are different from rain with $P<0.05$ with the exception of deep soil water which has $P<0.09$ of being different from rain water.

If the significance testing is repeated with reference only to sampling site then there may be a difference in concentration identified between Hexham 1 and Hexham 2 ($P<0.18$) – these are the most physically different grips. There is also a significant difference between Cowgreen and Hexham 2.

3.4.7.2 PC2

This component is the hardest to interpret, distinguishing primarily between high Ca or Fe and high K concentrations. This may suggest that the component is related to flow or season, with Ca and Fe being terrestrial elements concentrated under low flow conditions. The origins of K within these catchments are however less clear. Interpretation of PC2 as being related to flow makes sense in the context of the low proportion (10%) of variation in this component that is explained by differences between sites and the high proportion (56%) that is explained by differences between sampling dates. In light of the low proportion of variance explained by differences between sites it is not surprising that there are no significant differences between any of the Hexham sites. Some difference between Cowgreen and Hexham sites 2 and 3 could also be understood if PC2 is related to season: Cowgreen had a greater tendency to hold onto ponded water during dry periods, meaning that a greater proportion of samples from this site may be representative of low flows or summer conditions.

3.4.7.3 PC3

PC3 has been interpreted as the component most likely to distinguish systematic differences between the sites, separate from concentration or flow forcing. The proportion of variation (23%) in this component that is explained by the site factor is still low, especially compared to the 50% that is explained by the date factor. However the ω^2 values do indicate a large effect for the site factor and a smaller effect for the date factor.

Hexham 3 appears in this analysis to behave differently to the other three grips: relative to site and date, Hexham 3 is significantly ($P<0.05$) different to both Cowgreen and Hexham 2, and is the least likely to be different to deep soil water. Relative only to site there are no significant differences between any of the other three grips whilst Hexham 3 is different to each of Cowgreen ($P<0.005$) and Hexham 2 ($P=0.01$) and may also be different to Hexham 1 ($P=0.16$).

The PC1 vs. PC3 trends (Figure 3.28) also showed the behaviour of Hexham 3 to be different to Hexham 1 and 2 with the Hexham 3 trend having a shallower angle (more varied across PC3) than the other two Hexham grips. If PC3 represents differences in site behaviour then this suggests that Hexham 3 is less consistent in its behaviour (PC3 scores) than the other two Hexham grips. This could be understood in terms of Hexham 1 being a smaller, shallower catchment with a narrower range of flow conditions and behaviours (especially since water rarely ponded in Hexham 1, additionally narrowing the range of flow conditions over which samples were taken relative to the other sites) whilst Hexham 2 is the deepest and largest grip and also the only one unblocked, making it more likely to respond quickly to changes in soil water. Hexham 3 meanwhile is blocked, but is substantially larger than Hexham 1 and maintains flow and ponded water over a wider range of conditions. The closest physical comparison to Hexham 3 is Cowgreen; however the greater scatter of Cowgreen samples especially relative to PC1 makes comparison between Hexham 3 and Cowgreen difficult on these data.

3.4.7.4 d

The variable d was produced in an attempt to represent the differences observed visually between sites on the plot of PC1 vs PC3 (Figure 3.28). The high proportion of variation in this quantity (56%) that is explained by the site factor is therefore encouraging. However, although there appear in Figure 3.28 to be differences between the Hexham sites, the ANOVA results show that none of these are in fact significant, with the exception of Hexham 1 / Hexham 2 ($P=0.09$) when the effect of date is not considered. All grip sites and shallow soil water are significantly different from rain; however this does not reveal anything unexpected as the d values were calculated in terms of distance from the main rainwater trend.

3.4.7.5 General

Although there is some evidence of differences between the grip sites, this is not consistent. In terms of overall concentration, represented by PC1, the distinctions between sites vary depending on whether significance tests account for variation by site as well as date. Including both factors, the concentrations of all grips are different to rain but there is little to distinguish the grips. Excluding date, the blocked sites are similar to one another, but different to both the unblocked site and to source water. This suggests that these differences are due more to variations with time (or flow) than to any differences between the sites themselves. Apparent differences between the sites observed by visual examination of the PC1 vs PC3 score plot (Figure 3.28) were found not to be statistically significant. It is therefore not possible from these analyses to accurately characterise differences between the grip sites; other variations that may be due to season or flow mean that such a signal cannot be genuinely determined.

3.4.8 PCA: repeat excluding ponded water

The samples included in the PCA in the previous section were taken opportunistically on site visits, meaning that the samples were not taken with any regard to flow conditions and a significant proportion were taken when flow was in fact zero and water was ponded in the grips behind the weir plates. It could be argued that such samples are likely to represent, or at least be confounded by, separate processes of sample evolution within the ponded water, as opposed to differences in the nature of the solute production from the catchments themselves. This may in turn contribute to increased scatter in the observed samples which could obscure statistically significant differences in site behaviour.

In order to test this hypothesis the dataset was reduced by excluding those samples that were taken under conditions of no flow. It was also found in section 3.4.7 that the data did not allow reliable distinctions to be made between sites that could be said to be due to factors other than changes in flow or season. Excluding no-flow samples will also help to test the hypothesis that there are differences between sites, in that since low (zero) flow samples are excluded, and since these samples were primarily taken in summer, the effect of flow or seasonal forcing will be incidentally somewhat reduced.

The aim of this process was to exclude stagnant ponded water. However due to the uncertainty in flow measurements, especially in those grips where flow series were modelled rather than measured, the cut-off point was not set precisely to zero. Instead the cut-off point below which samples were excluded was taken as the median flow value for each site – given the flashy nature of the hydrographs this value is unlikely to exclude any runoff events but will eliminate ponded water. The cut-off values for each site are given in Table 3.15;

the rain and soil water samples were of course unaffected by this and the total number of samples for the PCA was 258. The significance of the correlation matrix was unchanged with all variables being significantly correlated ($P<0.05$) except K with Ca and Fe (Table 3.16).

PCA on the correlation matrix produced the eigenvectors shown in Table 3.17. The scree test (Figure 3.29) once again suggested the retention of three components and the loadings of these components were not greatly different to those in the PCA on all data (Figure 3.30 and Figure 3.31). Interpretation of the component loadings is therefore similar.

Site	Minimum flow cut-off (L sec^{-1})	N samples above cutoff
Hexham 1	0.015	20
Hexham 2	0.097	31
Hexham 3	0.046	29
Cowgreen	0.062	26

Table 3.15 Minimum flow values for samples in the second model

	Al	Ca	Fe	K	Mg	Na
Al	1					
Ca	**0.4451**	1				
Fe	**0.4554**	**0.3257**	1			
K	**0.363**	-0.0226	0.0961	1		
Mg	**0.5935**	**0.2994**	**0.3305**	**0.2178**	1	
Na	**0.6463**	**0.2653**	**0.2489**	**0.2916**	**0.8379**	1

Table 3.16 Correlation matrix for the variables after removal of ponded samples. Shaded cells indicate correlations significant at P<0.05

Variable	1	2	3	4	5	6
Al	0.5033	0.00858	0.15315	0.11095	-0.82249	-0.18537
Ca	0.30889	0.59195	0.06681	0.68128	0.28813	0.05061
Fe	0.32652	0.41111	0.51215	-0.64294	0.18595	0.11887
K	0.23468	-0.64473	0.60838	0.27242	0.29086	-0.01756
Mg	0.49356	-0.11779	-0.41876	-0.17802	0.34432	-0.64569
Na	0.49597	-0.22574	-0.40534	-0.06535	0.05251	0.7292
Eigenvalue	2.9567	1.09655	0.82556	0.65235	0.32307	0.14576
Difference	1.86015	0.27099	0.17321	0.32929	0.1773	.
Proportion	0.4928	0.1828	0.1376	0.1087	0.0538	0.0243
Cumulative	0.4928	0.6755	0.8131	0.9219	0.9757	1

Table 3.17 Results of the PCA on flowing samples

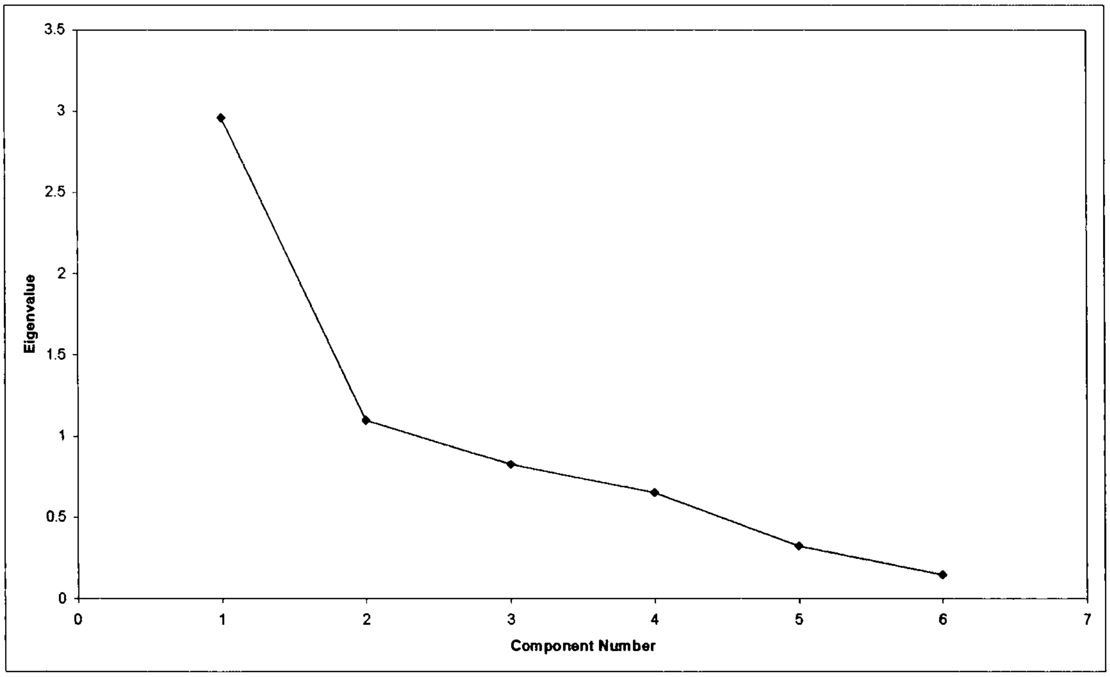


Figure 3.29 Scree plot of the eigenvalues for the PCA on flowing samples

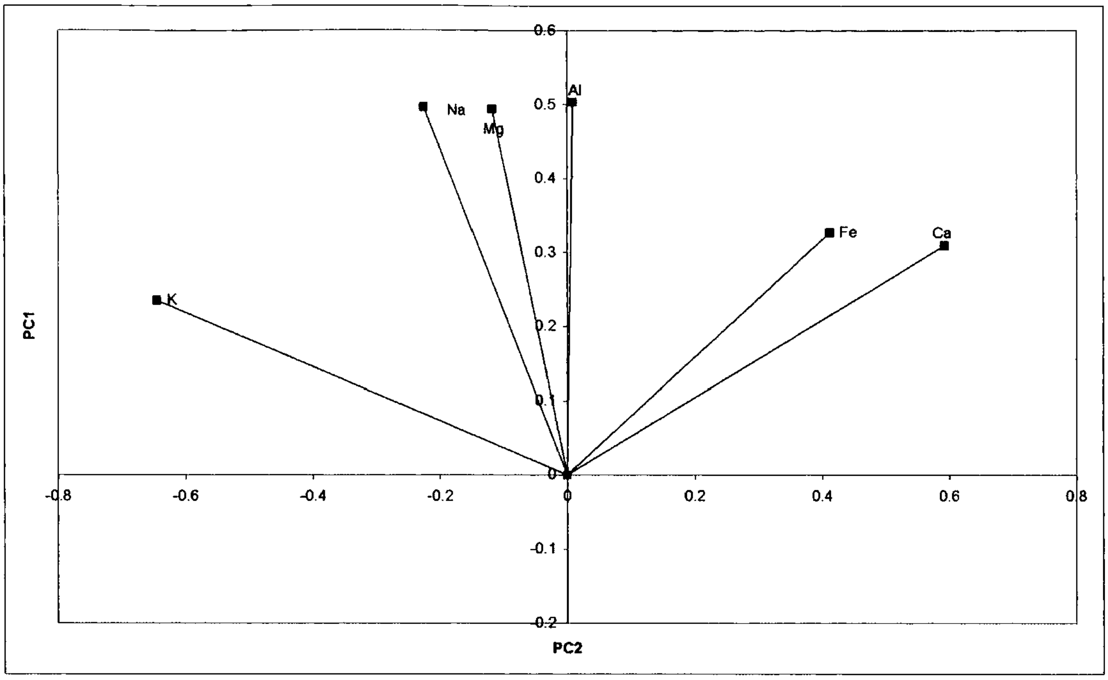


Figure 3.30 Loading plot of PC1/PC2 for the analysis on flowing samples

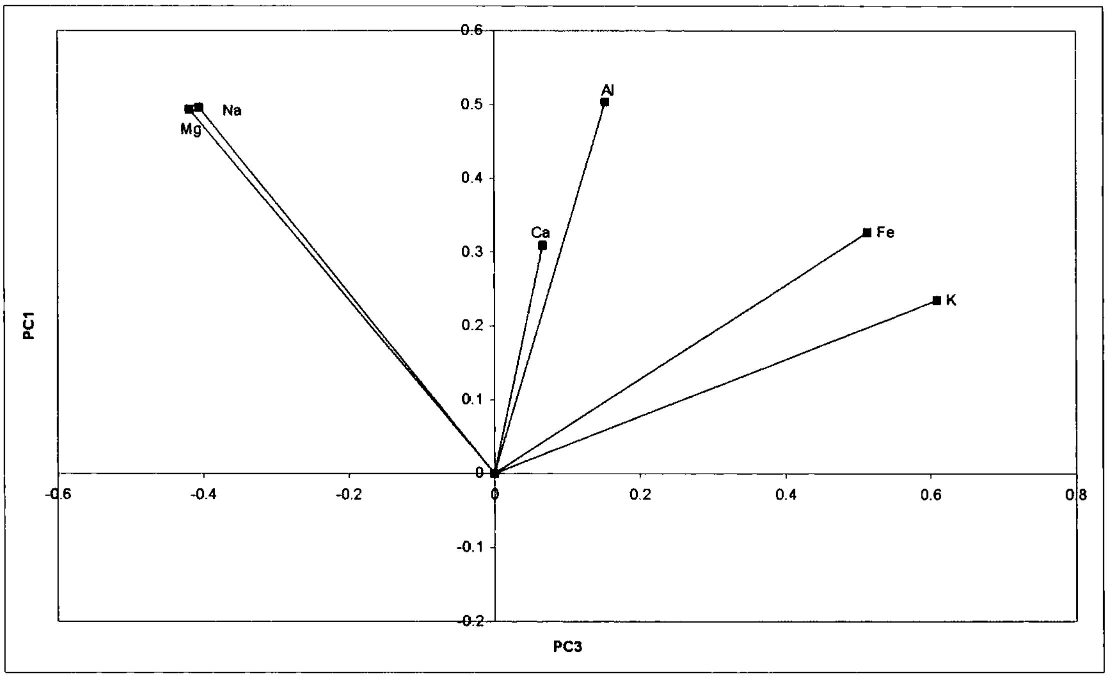


Figure 3.31 Loading plot of PC1/PC3 for the analysis on flowing samples

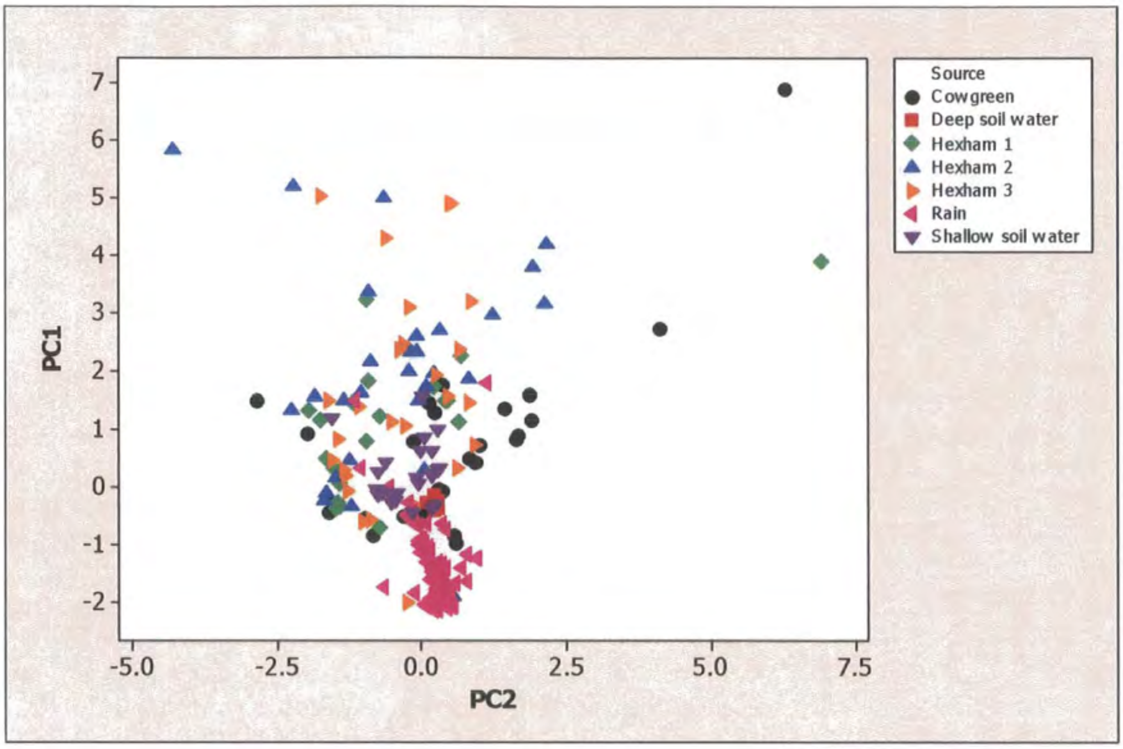


Figure 3.32 Score plot of PC1/PC2 for the analysis on flowing samples, grouped by site

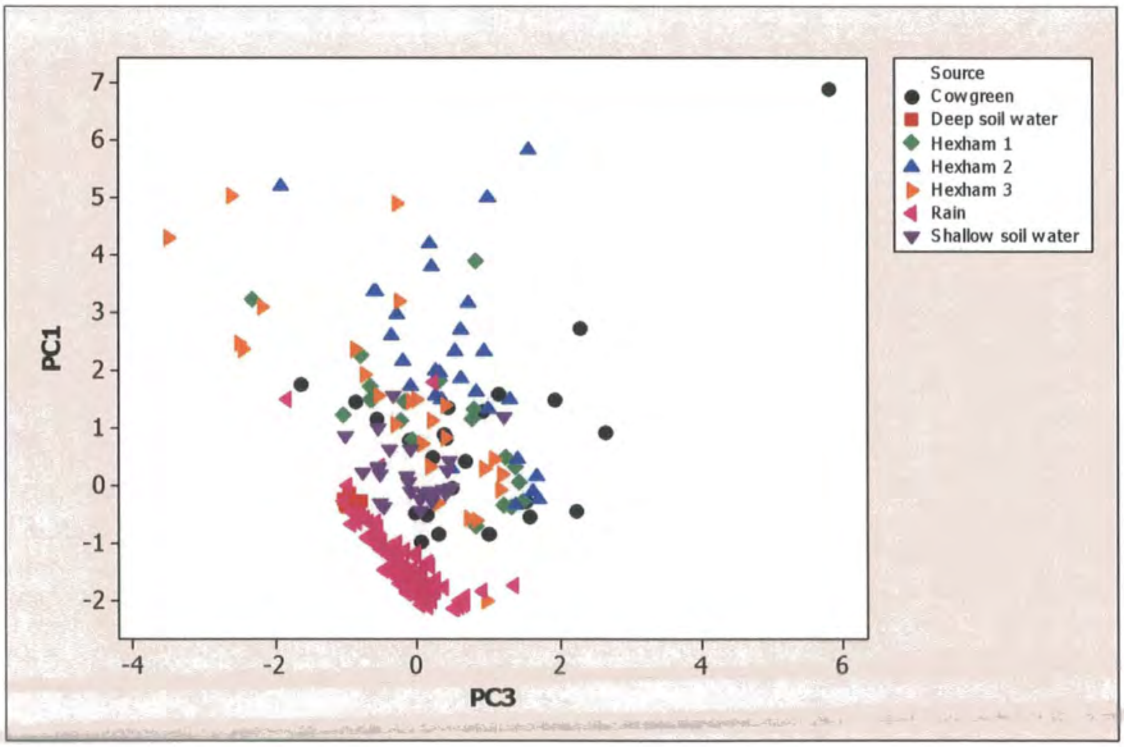


Figure 3.33 Score plot of PC1/PC3 for the analysis on flowing samples, grouped by site

The similarity in the loadings of this second PCA means that it is not surprising that for those samples which remain the overall form of the score plots is similar (Figure 3.32 and Figure 3.33). However, although the overall shape of the PC1 vs. PC3 score plot in particular is similar for this second analysis (Figure 3.33 vs. Figure 3.28), the shape is somewhat clearer due to the removal of some of the most scattered points, which can be seen to have represented ponded samples. It can now be more reasonably suggested that the samples do follow two key trends away from a low PC3 / negative PC1 rainwater end-member: the first trend towards negative PC3 / positive PC1, and the second trend towards positive PC3 / positive PC1 (Figure 3.33). With reference to the loading plot for these two components (Figure 3.31) these trends can be see to represent increasing Mg and / or Na, and increasing K, Fe, Al, and Ca respectively.

The scores of the points do not follow these trends closely enough to unambiguously identify three end-members which encompass all the other scores, but for the purposes of making general inferences about differences in behaviour between the grips, three samples can be selected which do include almost all of the grip samples and exclude only rainwater samples due to the scatter on the rainwater trend. The end-member points selected are shown in Figure 3.34 and Table 3.18. It is important to note that the fact that these end-members do not bound all the other samples, especially the rainwater samples, does mean that the analysis should not be interpreted too literally as a mixing of waters; however a general analysis in terms of the trends observed in each catchment is appropriate.

Sample source	End-member label	Al	Ca	Fe	K	Mg	Na	PC3 score	PC1 score
Hexham 3 01/05/2003	A	0.13	0.99	0.59	0	1.29	7.50	-3.48	4.30
Cowgreen 17/06/2003	B	0.18	2.89	15.30	0.07	0.75	3.29	5.80	6.91
Rain 03/12/2003	C	0	0.16	0	0.13	0	0.05	0.52	-2.12

Table 3.18 Composition of the three selected end-members. Solute concentrations in mg/l

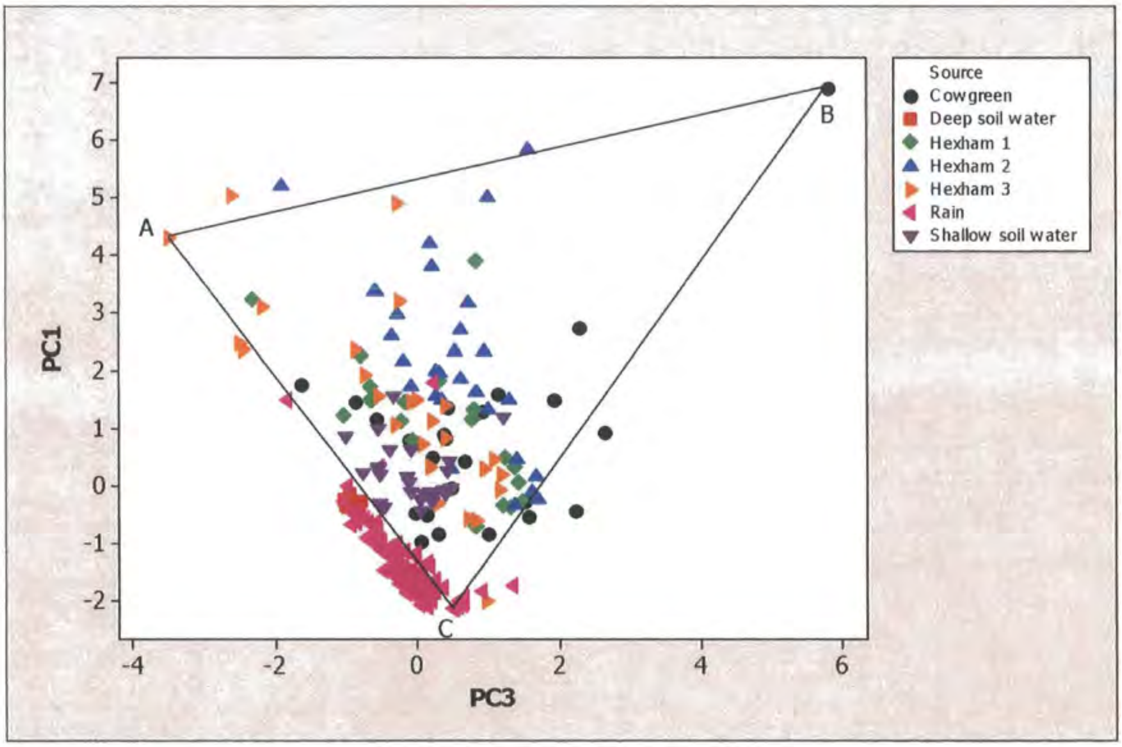


Figure 3.34 Endmembers selected for unmixing analysis

The composition of the samples falling within the end-member mixing lines in Figure 3.34 can be represented as proportions of each of the three end-members. The proportions of each end-member were calculated for each sample (further description of the method is given in section 5.6) and the proportions of each end-member were plotted over time for each site in order to visually identify differences between site behaviours. One disadvantage with this interpretation method is that the frequency of samples is not sufficient to identify individual flood peaks, and therefore to relate or observe the effect of individual storm events on the end-member proportions observed in the grips, except on those occasions where sampling happened to coincide with an event (for example 11/08/2004). However general patterns differentiating between drought periods (Summer 2003) and wet periods (especially October – December 2002 and October – December 2004) can be qualitatively identified (Figure 3.35, Figure 3.36 and Figure 3.37).

End-member A proportions are generally higher in all grips than in rainwater (Figure 3.35). End-member A represents high Mg and Na, and therefore rainwater samples that are relatively high in this end-member represent sea-salt events. The best example of this is the rainwater sample on 8/10/2003. However due to the infrequency of sampling, especially compared to the flashy nature of the hydrographs from all the sites, it is unfortunately not possible to make clear inferences about the influence of the chemistry of particular rainwater events such as this on the chemistry of the grip waters: the next flowing sample from Hexham 3 and Cowgreen after this event was taken on 29/10/2003 and from Hexham 2 on 05/11/2003.

A less extreme example of a rainwater event high in end-member A is 22/9/2004. On this occasion, samples were taken from the grips on the same day and the high end-member A proportion of the rainwater does appear to be matched by increases in each of the grips. However once again there is insufficient data to determine whether the grips differ from one another in their response to the high end-member A input.

The general increase in end-member A concentrations in the grips throughout summer 2003 therefore seems likely to be due to evaporative concentration of the waters in the grips: although ponded samples have been excluded from this analysis the flows were still low and sporadic during this period. The proportion of end-member A in Hexham 2 rises later than in either Hexham 1 or Hexham 3: this may be due to higher flows being maintained for longer in Hexham 2 causing evaporative concentration to have a lesser effect. Soil water samples appear to generally follow the same trends as the grip samples, with the exception of the rain and grip water sea-salt peak on 22/9/2004 which is not observed in the soil water samples. This may suggest that soil samples are somewhat buffered to changes in the input proportion of end-member A, demonstrating that the grip waters are influenced by rainwater to a greater extent than even the shallow soil water, presumably through the contribution of overland flow.

As most rainwater samples fell outside the region bounded by the selected end-members (Figure 3.34) the proportion of end-member B was not defined for these samples. The rainwater samples in general are therefore clearly low in the solutes contributing to end-member B, namely Al, Ca, Fe, and K. Of the occasions when the grips were sampled on the same day, Hexham 2 samples have a higher proportion of end-member B than either Hexham 1 or Hexham 3 on all but two occasions: 29/11/2003 (when Hexham 3 was higher) and 11/08/2004. These two dates may be significant because they both represent periods of high flow, and the event around 11/08/2004 in particular was a major storm event across the region. However, any systematic pattern is unclear from these two points with Hexham 3 being higher in the first instance and Hexham 1 in the second instance.

Samples with a high proportion of end-member C are, given the position of this end-member on the score plot (Figure 3.34) those with the lowest (most negative) PC1 scores, equating to a low overall concentration; high points on the end-member C plot (Figure 3.37) therefore represent samples with lower overall concentration. As would be expected from the ternary nature of the mixing diagram, the proportion of end-member C largely mirrors the major trends in the other two end-members: the proportion of end-member C is low throughout the dry summer of 2003, and the large storm of 11/08/2004 results in an increase in end-member C for Hexham 2 and Hexham 3.

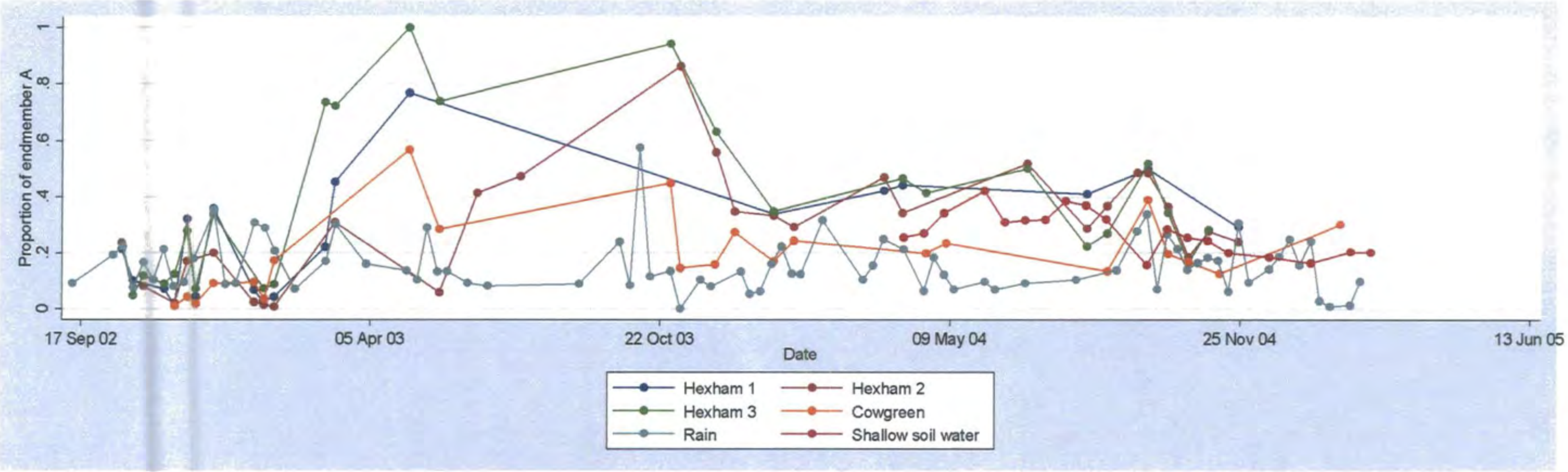


Figure 3.35 Proportion of end-member A over time for each site, for flowing samples only

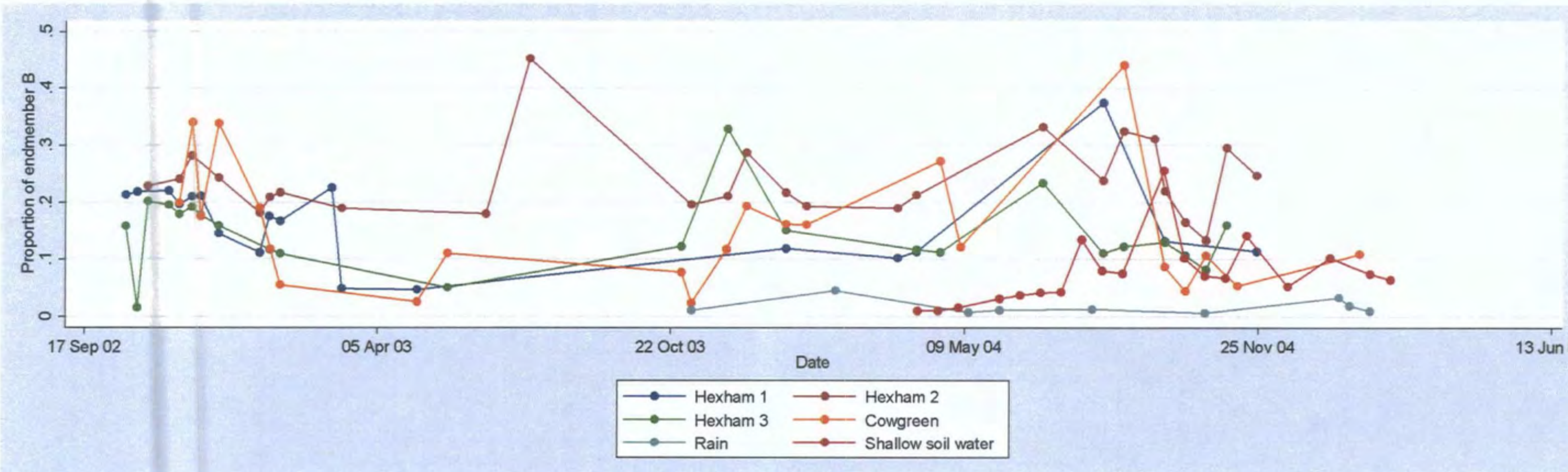


Figure 3.36 Proportion of end-member B over time for each site, for flowing samples only

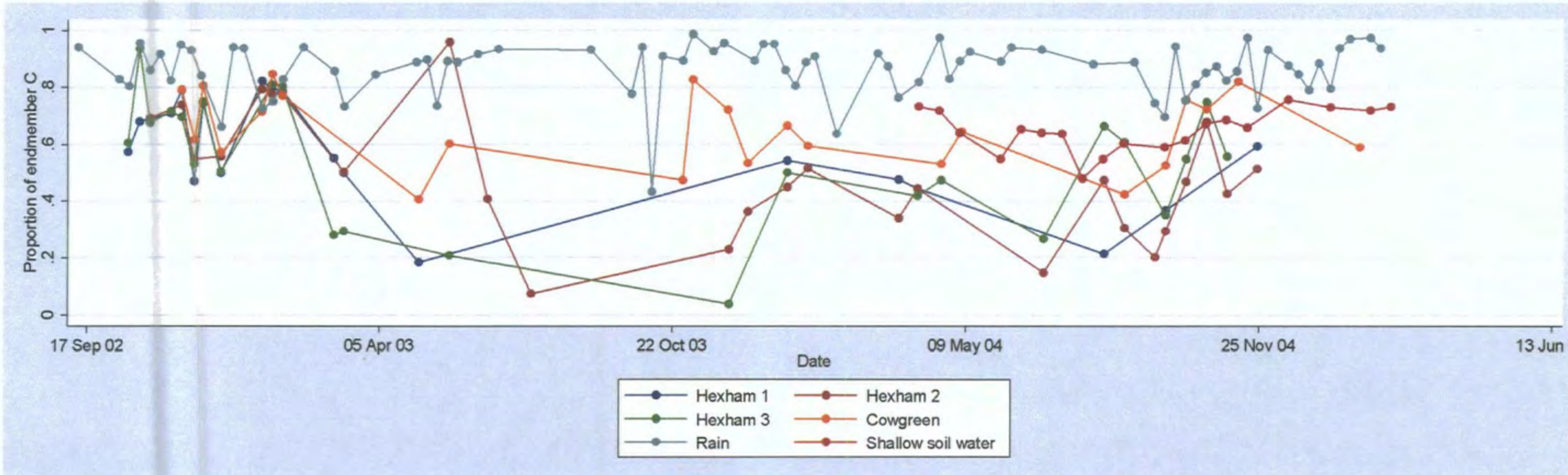


Figure 3.37 Proportion of end-member C over time for each site, for flowing samples only

In order to more rigorously examine the differences between sites, for each end-member the differences between sites were analysed using an ANOVA procedure with Tukey post-hoc significance testing, in a similar manner to the analysis described in section 3.4.7. In this case each end-member in turn was taken as the response variable. Fixed factors were once again the sample site and sample date, and the analysis was repeated with only sample site as a fixed factor. Results are presented in Table 3.19 – Table 3.26 with the same colour scheme of shading significant results to aid interpretation. Once again the effect of site was highly significant in all tests and so all Tukey post-hoc tests were performed.

2 factor	End-member A			End-member B			End-member C		
	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2
Site	0.00	0.24	0.23	0.00	0.45	0.43	0.00	0.54	0.53
Date	0.01	0.53	0.20	0.16	0.33	0.07	0.00	0.34	0.16
Error		0.22			0.22			0.12	

Table 3.19 ANOVA table for two factor analysis on end-members A, B and C

End-member A 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.21					
Hexham 2	0.18	>0.995				
Hexham 3	<0.005	0.41	0.24			
Rain	>0.995	0.24	0.21	<0.005		
Deep	0.04	0.77	0.64	>0.995	<0.005	
Shallow	0.60	>0.995	>0.995	0.43	0.16	0.34

Table 3.20 Post-hoc significance tests between sample sources, response variable end-member A

End-member B 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	>0.995					
Hexham 2	0.13	0.13				
Hexham 3	0.50	0.62	<0.005			
Rain	0.46	0.54	0.03	0.92		
Deep	n/a	n/a	n/a	n/a	n/a	
Shallow	0.30	0.40	<0.005	0.92	>0.995	n/a

Table 3.21 Post-hoc significance tests between sample sources, response variable end-member B

End-member C 2 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.31					
Hexham 2	0.07	>0.995				
Hexham 3	0.06	>0.995	>0.995			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	>0.995	0.82	0.60	0.59	<0.005	
Shallow	>0.995	0.56	0.24	0.23	<0.005	>0.995

Table 3.22 Post-hoc significance tests between sample sources, response variable end-member C

1 factor	End-member A			End-member B			End-member C		
	P	η^2	ω^2	P	η^2	ω^2	P	η^2	ω^2
Site	0.00	0.24	0.22	0.00	0.45	0.43	0.00	0.54	0.53
Error		0.76			0.55			0.46	

Table 3.23 ANOVA table for one factor analysis on end-members A, B and C

End-member A 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.69					
Hexham 2	0.14	0.99				
Hexham 3	<0.005	0.20	0.57			
Rain	0.74	0.02	<0.005	<0.005		
Deep	0.08	0.90	>0.995	0.92	<0.005	
Shallow	0.88	>0.995	0.81	0.03	0.02	0.58

Table 3.24 Post-hoc significance tests between sample sources, response variable end-member A

End-member B 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.99					
Hexham 2	<0.005	0.01				
Hexham 3	0.98	0.84	<0.005			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	n/a	n/a	n/a	n/a	n/a	
Shallow	0.01	<0.005	<0.005	0.06	0.17	n/a

Table 3.25 Post-hoc significance tests between sample sources, response variable end-member B

End-member C 1 factor	Cowgreen	Hexham 1	Hexham 2	Hexham 3	Rain	Deep
Hexham 1	0.45					
Hexham 2	<0.005	0.53				
Hexham 3	0.03	0.94	0.98			
Rain	<0.005	<0.005	<0.005	<0.005		
Deep	0.89	0.05	<0.005	<0.005	<0.005	
Shallow	>0.995	0.17	<0.005	<0.005	<0.005	0.99

Table 3.26 Post-hoc significance tests between sample sources, response variable end-member C

3.4.8.1 End-member A

Differences between sites explain only 24% of the variation in end-member A, whilst variation with date explains 53%. Increases in end-member A proportion correspond to increases in Mg and/or Na concentrations, and so increases in end-member A are in the same general direction as the main rainwater trend. Since differences between rainwater samples represent variation only by date, and not by site, it is not surprising that end-member A does not distinguish well between the grip sites and that the majority of the variation on this end-member is attributable to differences over time.

This is equivalent to saying that since variations in end-member A represent the main trend that is observed in rainwater, end-member A would only be expected to distinguish between the grip sites firstly if they differ in the response of their runoff chemistry to rainfall, or secondly if the composition of the rainfall at the sites actually differs from that in this dataset. Cowgreen is close to the site of the rainfall samples at Moor House whilst the Hexham sites are approximately 20km away and are more likely to have received different rainfall. This fact makes it difficult to make inferences about the difference between Cowgreen and the Hexham sites in terms of the end-member A proportion. As for the three Hexham sites, there appears to be little or no significant difference in the end-member A proportion.

3.4.8.2 End-member B

At a given concentration or PC1 score, the contrast between end-members B and A is primarily a contrast along PC3, interpreted in section 3.4.6 as the component most likely to distinguish differences in behaviour between the sites. Due to the position of the bounding end-members chosen in the unmixing analysis, no deep soil water samples were included in this analysis as they had negative end-member B scores, falling outside the region bounded by the end-members.

The only significant differences taking into account both site and date were between Hexham 2 and each of the other sites and sources. Hexham 2 differed from Cowgreen and Hexham 1 with P=0.13 in each case, and from Hexham 3 with P<0.005. Taking only sampling site into consideration, Hexham 2 differed from each of the other grip sites with P<0.01 whilst there were again no significant differences between any of the other grip sites.

These are important results as they appear to distinguish the unblocked site (Hexham 2) from each of the blocked sites, whilst the response on which the distinction is made (end-member B) is the one that has been associated with catchment behaviour and, from its strong association with Al and Fe in particular, is also likely to be associated with increasing DOC concentrations (DOC was not included in this analysis). Other response variables including those linked primarily to general concentration and to possible input forcing have not distinguished the grip sites in the same way.

Why does end-member B separate the grip sites in a way that PC3 did not? Two reasons seem likely. Firstly, the previous analysis included ponded samples, effectively increasing the noise in the data. Secondly, increased end-member B scores do not solely represent increased PC3 compared to end-member A: there is also an associated increase in PC1. A higher proportion of end-member B can therefore represent not only proportionate increases in Al and Fe (likely to be associated with increased DOC), but also an increase in overall sample concentration.

3.4.8.3 End-member C

End member C is closely related to PC1 scores: increases in proportion of end member C correspond to a more negative PC1 score. Increases in proportion of end-member C therefore represent decreased overall sample concentration. Consequently, similarly to the ANOVA on PC1 (section 3.4.7.1) this analysis distinguishes primarily between rain and all other samples. For the one-factor analysis, the significant relationships are very similar for PC1 and end member C (Table 3.11 vs. Table 3.26). The high proportion of variance in end member C (54%) that is explained by differences between sites is not necessarily instructive: rainwater samples would be expected to be of lower concentration or higher end-member C than any of the other waters. Because rainwater is counted as a "site" and as a source water is very different from any of the other sites in terms of overall concentration, a high proportion of variance on this end member being explained by "site" is to be expected. End member C proportions are not significantly different between any of the Hexham grips, emphasising that the differences observed for end member B between Hexham 2 and the other two Hexham grips are dependent on both PC1 and PC3.

3.4.8.4 General

In terms of assessing the extent of differences between the sampling sites, end member B provides the most useful information in these analyses. If sample date is not included as a factor then this end member identifies highly significant differences between the unblocked site Hexham 2 and all the blocked sites, which in turn are not identified as being different from one another. Although a proportion of this could be due to flows being maintained over different periods at Hexham 2, this is in itself important as it indicates a hydrological difference; it should also be noted that this analysis was conducted only for flowing samples in any case. Including sample date as a factor, this end member still identifies highly significant differences between the unblocked site Hexham 2 and the most physically similar blocked site, Hexham 3. Significant differences are also observed albeit with a lower probability between Hexham 2 and the other two blocked sites. This provides the first firm piece of evidence that there may be genuine differences between the blocked and unblocked sites, with the unblocked site being distinguished by a combination of increased Al and Fe, and an increased overall concentration. This is most likely to suggest (for the same reasons outlined in section 3.3.1) that Hexham 2 contains a higher proportion of deeper soil water, over a wider range of flow conditions, than the other grips.

3.5 Tracer based comparison of Hexham 2 and Hexham 3

3.5.1 Experiment outline

A final experiment was carried out with the specific aim of identifying any differences in the flow behaviour of the Hexham 2 and Hexham 3 grips. These two grips were selected (as opposed to Hexham 1) as they were the most similar grips in the study. Although the Hexham 3 catchment is smaller overall, the grip channels towards the lower end are of similar depth and width, except where the Hexham 3 channel is blocked. A tracer experiment was carried out over a period of approximately two weeks to monitor the appearance at the catchment outlets of a tracer introduced into the peat of the catchment.

As part of a separate experiment (not part of this study) that was conducted at the same field site, a dip-well transect was installed between the Hexham 2 and Hexham 3 grips. The transect was approximately 20m upstream of the monitoring points on the grip channels and was perpendicular to the two grip channels, consisting of four dip-wells evenly spaced between the channels. The dip-wells consist of drainage tubing of approximately 3" internal diameter, drilled with numerous holes along the length and inserted into the peat to a depth of approximately 1m, into holes that were pre-drilled with a soil auger. The dip-wells were installed in early 2003 and instrumented with pressure transducers for quasi-continuous water table measurement. By the time of the present experiment the dip-wells had been found to respond rapidly to changes in water table (J. Rowson, pers. comm.).

Flury and Wai (2003) provide a review of the many classes of tracer that can be used in hydrological studies. Key requirements for a suitable tracer are that it should behave conservatively (move in a similar manner to water, without extensive degradation, changes in behaviour dependent on water chemistry, or retardation through adsorption); that the background concentrations should be low; that suitable detection techniques should be available; and finally that the environmental impact should be minimal (Flury and Wai, 2003). Taken together, these requirements point to water itself being the ideal tracer molecule in hydrology, marked by either ^{18}O or ^{2}H isotopes, although detection facilities for these are expensive and were not available to the present study. Davis et al (1980) found the bromide and chloride anions to be among the best tracers for use in groundwater tracing, and Flury and Wai (2003) recommended bromide in particular, with chloride being appropriate to a certain extent but with the caveat that background concentrations of chloride are far higher than bromide and so detection of tracer breakthrough may be more difficult. Bromide, introduced as KBr, has been used with some success as a tracer in peat soils, for example by Baird and Gaffney (2000) and Gafni (1986).

For this experiment a solution of potassium bromide was used as the main tracer. 1 kg of potassium bromide was dissolved to saturation concentration in milli-RO purified water. This solution was introduced in equal quantities to each of the four dip-wells on the transect between Hexham 2 and Hexham 3. At the same time 1kg of potassium chloride was applied as dry powder in an even line to the peat surface adjacent to the transect. The tracers were introduced this way round because background concentrations of chloride were expected to be much higher than bromide due to the greater environmental abundance of chloride. Due to the prevalence of overland and near sub-surface flow during storm events in the catchments, it was hoped there would be a better chance of observing a chloride peak if it was placed where the flow was expected to be most rapid. At the same time that the tracers were introduced the auto-samplers were activated on a two-hour sampling cycle; the site was then visited every two days to collect samples and restart the samplers.

Once collected samples were returned to the laboratory and filtered using individual 0.45μm syringe filters. Samples were then refrigerated before analysis (within four days) using a Metrohm ion chromatograph in conductivity-sensing mode. Standards were prepared using a serial dilution and were regularly re-analysed after approximately every 10 samples. Data were processed using the automatic peak identification in the Metrohm IC Net software and all peaks from both standards and samples were manually checked before the data were processed to create the calibration to solute concentration.

3.5.2 Results

Bromide and chloride concentrations observed in the samples are shown in Figure 3.38. Note the different y axis scales: as expected the background concentrations of chloride were much higher than those of bromide, which was only observed at extremely low concentrations. Observed concentrations were, however, well in excess of the limits of detection which were found to be in the region of 0.005 mg l^{-1} (C.D. Johnson, *pers. comm.*). Rainfall at the site is also shown; no significant rain occurred until almost a week after tracer introduction, when there was sustained low intensity rainfall over a period of approximately two days. There was a gap in sampling from 238 – 262 hours when a visit to the site was unfortunately not possible.

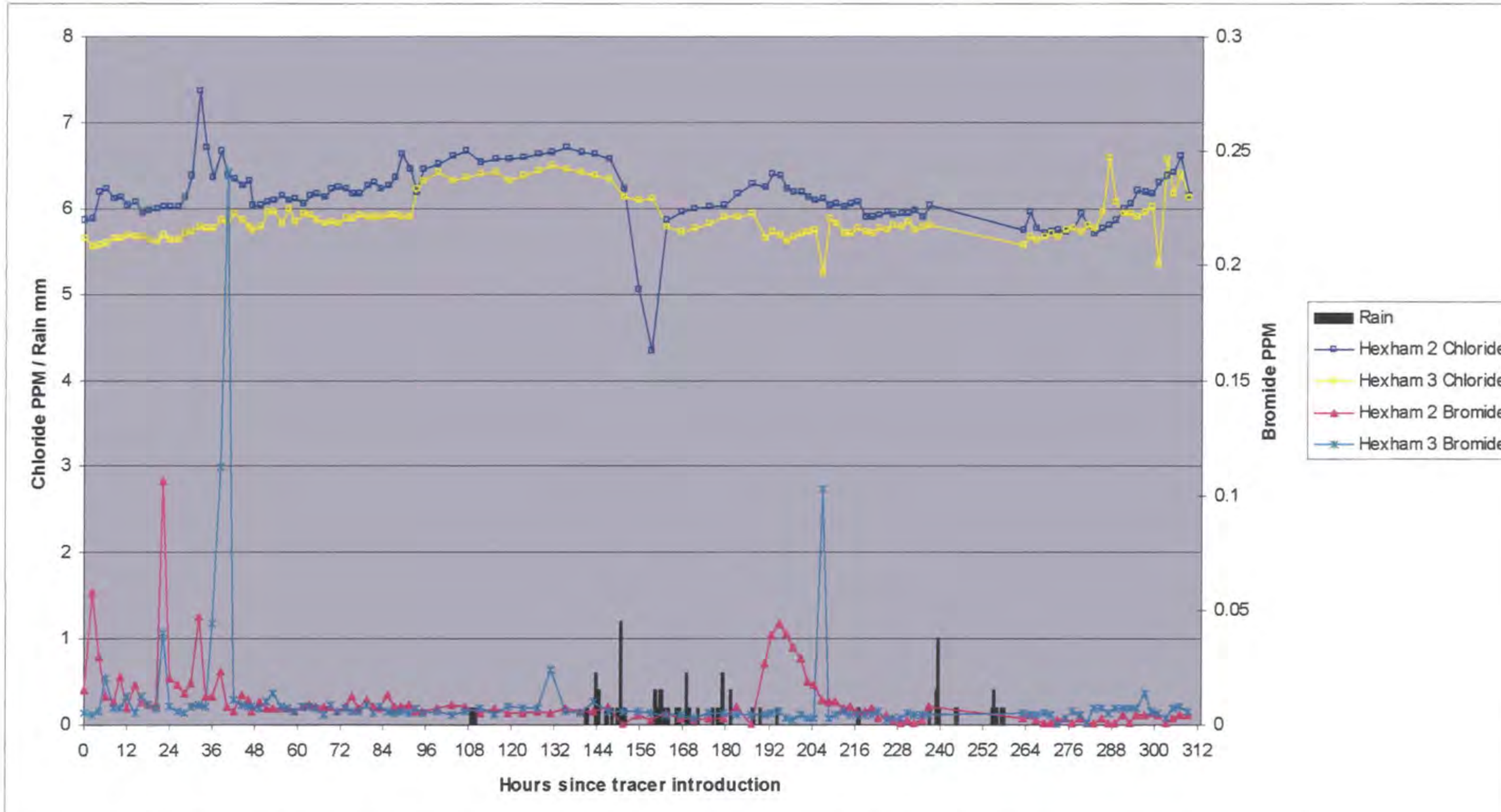


Figure 3.38 Results of the tracer monitoring for both grips

In Hexham 2 there is a small series of peaks in the bromide concentration over the 36 hours following tracer introduction. These are followed by a small peak in chloride in Hexham 2 at the end of this period. In Hexham 3 there is also an initial bromide peak, which occurs over a shorter period (two samples) but is much higher. No real peak is similarly observed in the chloride concentration of Hexham 3. After 48 hours concentrations of both tracers in both grips appear to have returned to background levels.

Two possible explanations are suggested for these results from the first 48 hours. Firstly, the initial peaks in bromide concentration could be due to rapid near-surface flow in the peat, either through macropores or diffusive flow, and not necessarily along the shortest physical path to each channel but also down the catchment. Since the dip wells were drilled at all levels right up to the peat surface, the bromide tracer was effectively introduced at all depths – not exclusively into the deep peat. In this case the arrival of the bromide in Hexham 2 prior to Hexham 3 may suggest better connectivity with a macropore structure in Hexham 2.

Alternatively, these bromide peaks may be due to bromide transport along the shortest path to each grip channel, through similar soil flow pathways for each grip but from only the two dip wells nearest to the grip channels. In this scenario the later peaks would then represent the tracer from the two dipwells furthest from the channels.

The first explanation has particular merit in that transport through diffusion or through macropores in the peat need not be affected by the blocks in the grip channel which, if the second explanation is true and bromide travelled directly to the grip channel and then along the channel, would mean the tracer would be likely to be retarded in Hexham 3 by the block pools.

At approximately 150 hours after introduction there is a substantial drop in chloride concentration in Hexham 2, which is not observed in Hexham 3. This points to dilution of background concentrations by the rainfall and suggests that the introduced chloride was not significantly observed in either grip. The lack of a drop in Hexham 3 therefore fits with the suggestion made in section 3.3.2 that the pools behind the blocks in Hexham 3 cause rainfall to have a delayed or step-change effect on concentration, which this rainfall was not sufficient to trigger.

At approximately 180 hours after introduction, and after substantial rainfall, there is a longer-lasting pulse of bromide observed in Hexham 2, which is followed by a higher but shorter (only one sample) peak in Hexham 3 at 204 hours. A similar peak is not observed for chloride in either grip but given the vastly higher background concentration of chloride and the scale of the bromide peak relative to this, this is not necessarily surprising as bromide and chloride were introduced in the same quantity. Once again the possibility of the block pools in Hexham 3 buffering the change seems likely, with the bromide arriving in the two grip channels upstream at similar times, but in Hexham 3 being retarded by the pools. The sudden appearance of bromide in the channel below the blocks could then occur once a certain quantity of flow has passed through the pools. If this is correct then a further increase in bromide in Hexham 3 would be expected with further storm events of sufficient magnitude. The rainfall around 240 and 252 hours may have been sufficient but unfortunately this was during the gap in sampling.

The likely retarding effect of the block pools means that it is difficult to define differences in the behaviour of the catchments in terms of the speed of transport through the peat to the grip channels. However this study is primarily concerned with export from the catchments as a whole, rather than in-soil transport processes and as such the suggestion that the grip pools both retard and then cause a step change in export concentrations is certainly relevant.

3.6 Conclusions

This chapter has presented the results of a series of independent experiments conducted to test the hypothesis that there are differences between the five catchments in the study which are attributable to blocking of the grips.

Early results indicated (section 3.2) that the pristine stream catchment behaved in a very different manner to any of the grips, with at least two old water end members representing peat runoff in addition to water that had contacted an alkaline source such as limestone. This difference meant that further experiments were conducted only on the four grip catchments; the analysis of pH and conductivity did not reveal any major differences between the blocked and unblocked grips; only one grip (Hexham 3) had a significant ($P<0.05$) pH vs. conductivity relationship and even here the difference was not large.

Taking conductivity as a proxy for concentration (from a single rainwater source), quasi-continuous monitoring of conductivity in the unblocked catchment and the most similar blocked catchment was then used with flow data to assess the hysteresis in the old vs. new water runoff response over several storm events of varying magnitude in summer and autumn 2004. A mixture of Class 2 and Class 3 hysteresis was observed; which of these occurred was suggested to be linked to the intensity and scale of a storm, as well as the antecedent conditions. Wet antecedent conditions were related to Class 2 events, suggesting a quick response of old water, whilst drier conditions produced Class 3 events suggesting a delay in re-wetting of the peat or in dissolution of material. Class 2 events were more prevalent and overall conductivity was always higher in Hexham 2, illustrating that Hexham 2 accesses deeper or more dominant soil water sources, but there was nothing to suggest that this was caused other than by the somewhat larger scale and possibly depth of the Hexham 2 catchment. The hysteretic behaviour of Hexham 3 was somewhat more complicated than Hexham 2 and this was related to the presence of substantial pools behind each of the blocks in the grip channel, which could either buffer the input of new water in an event, or cause it to be “falsely” high prior to an event and then drop suddenly as the old water in the pools was flushed through.

Thirdly a multivariate analysis was conducted on the concentrations of base metal cations in grab samples taken from each of the grips, in addition to samples of precipitation and soil water at Moor House. Analysis of all the samples taken over the study period included samples taken of ponded water, and although there appeared to be mixing trends in the sample compositions and also differences between the grip sites, these were found not to be statistically significant. However, analysis of only those samples taken when the grips were flowing removed some of the scatter from the data and made interpretation easier. Although genuine mixing end-members were not found there were clear mixing trends and a qualitative mixing analysis was undertaken. In terms of an end member that represented a combination of Al and Fe and overall sample concentration, this analysis found statistically significant differences between the unblocked grip (Hexham 2) and all the blocked grips, with the unblocked grip containing a significantly higher proportion of this end-member. This result suggested Hexham 2 to show a higher concentration of soil water, rather than necessarily a different type of water.

Finally a simple tracer experiment was conducted with the explicit aim of testing the hypothesis that there are differences between the grips. The intention was to use separate tracers to identify surface and whole-peat (all levels) flow but due to limitations in analytical facilities the chosen surface tracer (chloride) could not be reliably identified against background concentrations. However the other tracer (bromide) was successfully observed in both catchment outlets, albeit at low concentrations. The results showed two separate peaks in each grip, of which the first seemed likely to be due to macropore flow and the second due to lateral transport through the acrotelm into the grip channels. The main (second) tracer pulse was observed in a more extended and somewhat earlier peak in the unblocked grip. The difference between the two grips for this second peak was suggested to be due once again to retardation of the water in the grip channel in Hexham 3 by the pools behind the grip blocks.

Taken together the results of these experiments do not present compelling evidence that there are differences between the grips in terms of the production of solutes. The strongest evidence for such a difference comes from the end-member analysis, but the hysteresis analysis shows that such differences may be due to physical differences meaning that Hexham 2 samples deeper water in any case. Therefore such differences are in terms of an increased concentration, in Hexham 2, of the same solute chemistry. All the other experiments suggest that the real differences between the grips lie in terms of their hydrological response; a result that is in accord with the differences in the DOC export budgets presented and discussed in chapter 2. This hydrological difference seems most likely to be due to the physical retardation of water that is caused by the pools that form behind the block channels. The best focus for further work will be to conduct a more detailed and extended tracer experiment across a larger number of catchments. This should include sampling over a larger number of storm events at different times of year, including the autumn flush period. The pools behind the blocks should also be sampled to develop a better understanding of the retardation of the water that these cause, and DOC should be sampled concurrently so that comparisons between tracer and DOC transport can be made.

4 Sources of DOC at the river catchment scale

4.1 Introduction

The originally observed trend that led to the inception of this study was one of increasing colour levels in rivers (Figure 1.1). Moorland drainage was proposed as one possible factor contributing to this trend, and chapters 2 and 3 presented the results of a detailed monitoring programme on a number of drains and assessed the potential benefits of blocking these drains. However, the DOC export from drains must be understood in terms of its effect on the overall DOC levels observed in the river catchment and thus the net export from the catchment.

This chapter presents the results of a series of experiments conducted to locate the main water colour source areas within the catchment of the River Tees above the Broken Scar water treatment works. From these results, relationships are determined between DOC concentration produced from subcatchments and the spatial and anthropogenic characteristics of those catchments, including peatland drainage, in order to develop a predictive model of DOC export. A range of statistical techniques for deriving these relationships are compared in order to assess the reliability of this and other studies.

4.1.1 Description of the River Tees catchment

The catchment of the River Tees above the Broken Scar water treatment works is largely rural in character, with an area of 818km^2 and elevation ranging from 36 to 889m. The location and elevation of the catchment is shown in Figure 4.1.

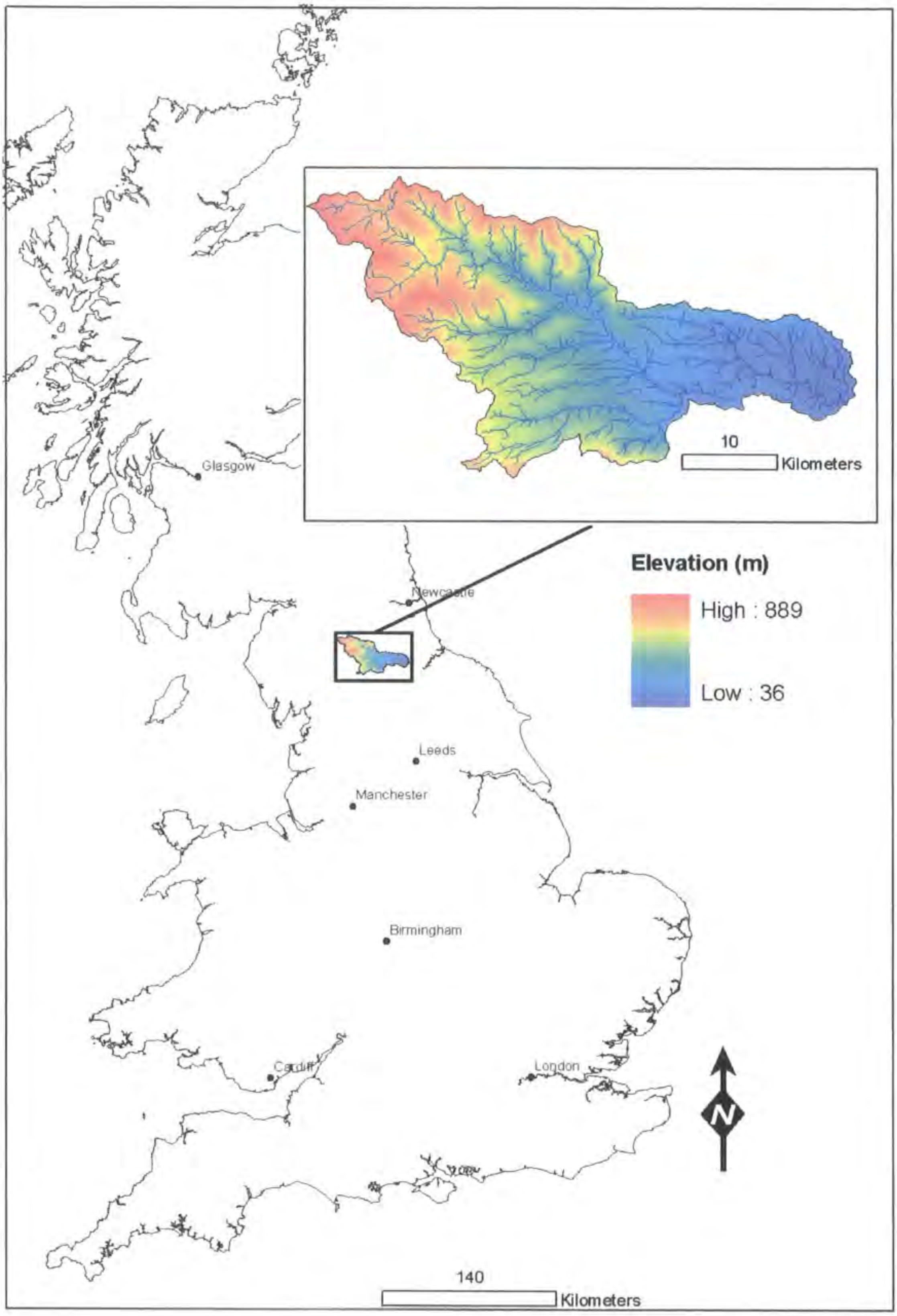


Figure 4.1 Location and elevation of the River Tees catchment above Broken Scar.

Data source © Crown Copyright/database right 2005. An Ordnance Survey/EDINA supplied service

The headwaters are predominantly in upland peat which is underlain by interbedded Carboniferous limestones and sandstones (Johnson and Dunham, 1963). There is a significant variety of relief across the headwater areas with several tributary streams to the north of the catchment being relatively steep, while other tributaries towards the south include extensive flat areas, such as Sleightholme Moor and Cotherstone Moor. The lower reaches of the catchment are predominantly low relief agricultural land which is underlain by Permo-Triassic sandstones.

A variety of catchment management and farming practices are found, from the parts of the catchment which fall within the Moor House NNR and are being managed as pristine blanket bog, to lowland, intensively grazed and cropped areas. The largest town within the catchment is Barnard Castle, with a population of approximately 5300.

4.1.2 Solving the problem – tracing the source

The present trends in water colour suggest that the Broken Scar water treatment works, along with other works on rivers elsewhere where similar trends are observed, may not be sustainable as a point will be reached when the colour load in the river water cannot be removed by the "end of pipe" solutions currently in use and under development. For this reason, there is a growing desire to address the problem at source by developing a better understanding of the main factors leading to colour production, enabling identification and treatment or exclusion from the water supply of key source areas. This chapter will aim to locate the main source areas of colour within the Broken Scar catchment through regular sampling campaigns of tributaries around the catchment. The colour production and other sample characteristics will then be related to spatial and land-use characteristics of those areas in order to develop a predictive model for colour production based on spatial and land-use data.

4.2 Context of the study

4.2.1 Prior studies

Several studies have previously monitored DOC concentration or water colour in streams with the aim of associating the amount of DOC exported from a catchment with a range of catchment morphometric properties and other characteristics such as soil types. In particular, a range of studies have suggested a correlation between DOC concentration and/or DOC flux, and some measure of the soil carbon content.

Eckhardt and Moore (1990) sampled a total of 42 streams in Quebec, Canada. Based on five sampling dates the DOC concentration in the streams showed a significant relationship to wetland cover, whilst the other morphometric variables studied (drainage rating, forest cover, catchment slope, and catchment area) did not improve the model developed between wetland cover and DOC concentration. Hope et al (1997b) compared average DOC concentration in 11 Scottish catchments with percentage peat cover, catchment area, altitude, and average slope. The study also monitored flow conditions and so was able separately to compare DOC concentrations sampled under storm conditions and under non-storm conditions. The study found significant correlations between average DOC concentration, and percentage peat cover and altitude. Catchment area and average slope were not significantly correlated (at the 95% level or better) with DOC concentration. (Hope et al., 1997b) Significant linear regression models were found between percentage peat cover and DOC concentrations (both including and excluding storm conditions) but including catchment area or altitude did not improve the models.

Aitkenhead et al (1999) studied 32 catchments ranging in size from 0.52km^2 to 150.25km^2 which were sampled on 12 occasions, all in summer, and compared mean DOC concentrations to: soil carbon content (determined from three separate sources, of which one was of a lower spatial resolution and was not found to be significant in any of the models); percentage peat cover; and catchment slope. The 32 catchments were divided into classes by size: small (<5km^2), medium (12-38km^2) and large (50-56km^2). For all catchment sizes taken together, a significant linear relationship was found between the DOC concentration and both the catchment soil C content and percentage peat cover, whilst no relationship was found between DOC concentration and slope. For "small" catchments similar relationships were found, in addition to a weak relationship between DOC concentration and slope. For "medium" catchments the relationship with soil carbon content was less significant and there was no relationship with percentage peat cover. For "large" catchments there was once again a significant relationship between mean DOC concentration and each of percentage peat cover and soil carbon content, in addition to slope (Aitkenhead et al, 1999). At all catchment scales except "medium" and for all significant predictors, lowland catchments plotted above the regression line (higher DOC concentration for a given predictor value) and upland catchments plotted below the regression line suggesting that for a given carbon pool, lowland catchments had a higher export of carbon to upland catchments. This was suggested to be due to land-use differences, such as greater forestry and agriculture in lowland catchments. The regression relationships explained the greatest amount of variance in DOC concentration in the case of small catchments and this was suggested to reflect the simpler nature of these catchments which contain less variation in other unexamined factors such as land use (Aitkenhead et al, 1999). The study concludes that soil carbon content is a good predictor of DOC concentration, and that in smaller catchments in particular peat cover is a good proxy for soil carbon content.

In contrast, Eatherall et al. (2000) studied 18 sites within the Swale catchment in Yorkshire, and found no significant relationship between DOC load and catchment soil organic carbon content. However this data was obtained over a particularly dry summer and the catchments included point sources of DOC such as sewage treatment works in addition to non-point sources such as high organic carbon content soils (Eatherall et al. 2000). This study may therefore be less representative of any true signal between soil carbon content and DOC load, firstly as the signal may have been weakened by the continuing effects of the dry summer and secondly due to the "noise" introduced by the point sources of DOC. Aitkenhead and McDowell (2000) have drawn a strong correlation between soil C:N ratio and the riverine flux of DOC. This correlation was drawn on large, biome-scale datasets and then extended to large watersheds.

Mitchell and McDonald (1992, 1995) sampled 45 streams within three major subcatchments of the River Burn, North Yorkshire, UK. Sampling was conducted on fourteen occasions within one year and over a range of flow conditions (although each individual sampling run was conducted as a "snapshot" with minimal change in flow conditions between the sampling of each stream). Mitchell and McDonald (1995) then proceeded to compare water colour to 32 catchment spatial characteristics or morphometric variables (Table 4.1) in addition to measures of the soil type, with the aim of identifying the characteristics having the most significant effect on colour export. To this end Mitchell and McDonald (1995) correlated each of their catchment characteristic variables with water colour and also developed linear regression models. Two variables were significantly correlated with the mean colour from each catchment across the fourteen sampling runs: the percentage of the total channel length found in areas with slope $<5°$ (%TCLA5°), and the percentage of the catchment with Winter Hill soil association cover (the Winter Hill soil association is deep, acidic blanket peat). A regression model was produced by stepwise selection of variables and this also included percentage Winter Hill peat and %TCLA5° and identified main stream slope as significant as well.

Overall Mitchell and McDonald (1995) identified low catchment slope, a high percentage of streams being present in areas of low slope, and the presence of winter hill peat as being the most significant predictors of high colour export.

Name / abbreviation	Description
Area	Basin area, km^2
Perimeter (Per)	Basin perimeter, km
$Elev_{max}$	Highest elevation in the basin (m a.s.l)
$Elev_{min}$	Lowest elevation in the basin (m a.s.l)
A5°	Area (km^2) with slope < 5 degrees
%A5°	Percentage of total area that has slope < 5 degrees
A3°	Area (km^2) with slope < 5 degrees
%A3°	Percentage of total area that has slope < 3 degrees
Basin relief (BR)	Basin relief or elevation range (m)
Basin Length (BL)	Horizontal distance of line from basin outlet to basin summit
Main stream slope (MSS)	Mean slope between 10 and 85 percentiles of main stream's length
Elongation (Elgn)	$(2^*Area^{0.5})$ / BL
Crenulation (Cren)	Per^2 / Area
Relief Ratio (RR)	BR / BL
Relative Relief (RRf)	Area / Per
Drainage density (DD)	TCL / Area
Geometry number (GeoN)	Area / DD
Total channel length (TCL)	Total channel length of all Strahler first, second, and third order streams as denoted on OS map (km)
Main channel length (MCL)	Length of the highest order stream in the basin (km)
N1st	Number of first order streams
N2nd	Number of second order streams
N3rd	Number of third order streams
Stream frequency (SF)	(2*N1st-1) / Area
Drainage intensity (DI)	SF / DD
Bifurcation ratio (BRt)	N1st / N2nd
Aspect (Asp)	Degrees deviation from north (implies W=E)
Springs (Spr)	Number of springs shown on OS 1:25000 map
CLA5°	Channel length in area of slope <5°
%TCLA5°	Percent of TCL that is in area of slope < 5°
CLA3°	Channel length in area of slope <3°
%TCLA3°	Percent of TCL that is in area of slope < 3°

Table 4.1 Morphometric variables studied by Mitchell and McDonald (1995), reproduced from that paper

Identification and measurement of a small number of catchment characteristics such as mean slope or percentage peat cover is practical to do manually from maps. However, the manual derivation of a large number of characteristics as in Mitchell and McDonald (1995) is time consuming and laborious. Foster and McDonald (2000), showed how the spatial analysis capabilities of GIS systems can be used to aid the rapid processing of spatial datasets to produce these statistics for any given area, through logical combination of existing mapping layers to create new layers, and extraction of data from each layer based on catchment zones. The study of Foster and McDonald (2000) also demonstrated that the use of GIS to classify catchments in this manner provides a tool to identify diffuse pollution sources. Since discoloured water can be seen as a type of diffuse source pollution, Foster and McDonald (2000) followed the predictive model developed by Mitchell and McDonald (1995) and used the GIS to identify areas where the soil type was winter hill peat and where the slope was less than 5 degrees, thereby identifying "pollution hazard" areas and enabling the assessment of the risk to the water supply from colour as predicted from the model developed in Mitchell and McDonald (1995). This demonstrates the creation of models for "hazards" such as predicted colour export and then the subsequent application of such models to other catchment areas, to produce hazard maps which can be readily understood and deployed across an organisation such as a water company that is seeking to mitigate or quantify the hazard, whilst also being easy to update following changes in the underlying model or data used.

4.2.2 Contribution of this study

This work aims to combine aspects of all these studies in order to develop and test a predictive GIS-based linear regression model for the colour export from any given area of the catchment, based on a series of spatial datasets that will be collected as part of the study. This work will extend the studies described above by seeking to develop a predictive model – it will be developed from a series of sampling runs to quantify the DOC concentration of exported water in terms of spatial variables. Since these variables can be derived for any arbitrary area in the GIS, the model will then be used to predict DOC concentration from other areas and identify areas contributing high DOC concentrations. The model will then be validated by the selection of new, previously unsampled, catchments, which will be sampled in order to test the predictive ability of the model, and the model will be refined.

The prime motivating factor for this study is an analysis of the source areas of the water colour that is observed at the water treatment works at Broken Scar, Darlington, England (Chapter 1). The colour observed at the water treatment works at any one time can be seen as a combination of the colour influences of all the upstream tributaries. Therefore at any one time, some tributaries will be contributing water of a lower DOC concentration than the final mix observed at Broken Scar, and other tributaries will be contributing water of a higher DOC concentration than observed at Broken Scar. The implication of this is that by comparison with the colour observed at Broken Scar, samples from other sites can be classified in a binary manner, as either contributing to or diluting the final downstream colour. This indicates the development of a binary logistic regression model which, similar to the linear regression model, can then be applied to arbitrary areas to predict which areas are net sources of colour which contribute water which dilutes the overall colour. Again, such a model will be validated and refined by the selection of new sampling sites. It is envisaged that such models would be of use to those involved in the evaluation of intake management strategies, in addition to allowing better application of catchment management-based remedial measures (Foster and McDonald, 2000) such as grip blocking, depending on the contributory variables identified.

4.2.3 Study outline

The field study consisted of a series of water sampling campaigns, each conducted on a single day across the catchment and numerous subcatchments of the River Tees above the Broken Scar water treatment works. Samples were analysed for a number of characteristics to quantify colour load, as modelled in this chapter, and water source types (as modelled in chapter 5). A range of spatial datasets for the Broken Scar catchment was collected and derived, and GIS-based catchment and statistical analysis was used to relate the sample characteristics to the source catchments.

Previous studies such as those outlined above have sought to identify relationships between catchment characteristics and the exported colour. This has typically been through statistical techniques such as correlation analysis and multiple linear regression. This study develops models in the context of an assessment of how appropriate these statistical techniques are to the datasets used: models are developed using a number of different regression techniques and the results and validity of these is discussed.

During the initial phase of the work, a predicted colour export model is produced, based on different variable selection techniques in multiple linear regression modelling, to be applicable to any given unit area and to previously unsurveyed subcatchments. In addition to this, logistic regression models are used to relate exported colour to the colour observed at the catchment outlet, in order to classify areas and subcatchments as having either a diluting or a contributing effect to the overall colour observed at the water treatment works. All models were then developed by further sampling runs and and the collection of a wider range of catchment descriptors. Finally the use of the new technique of Partial Least Squares regression is introduced as an alternative and more statistically justifiable modelling method.

The derived models will enable the better focussing of catchment remediation strategies, such as grip blocking and burn management, into those areas where the resultant improvement to observed colour at the water treatment works will be greatest.

4.3 Sampling programme

4.3.1 Sampling sites chosen

Sampling sites were chosen initially to cover as large and varied a set of subcatchments as possible, within the consideration that it should be possible to conduct a complete sampling run in a single day to minimise the change in conditions between samples. The River Tees itself was sampled as close as possible upstream of Broken Scar, as this was taken to be the catchment outlet, providing the water relative to which all the other samples were to be compared and subsequently classified as diluting or concentrating in terms of DOC levels. Next, sites were chosen to include all major tributaries to the Tees throughout the catchment, including the River Greta, River Balder, and the River Lune, as well as several smaller tributaries feeding directly into the Tees, such as Hudeshope Beck and Eggleston Burn. Finally a range of sub-tributaries were also chosen to include as wide a variety as possible of catchment characteristics such as peat cover, slope, and altitude.

Sampling was an iterative process with different combinations of sites being sampled on each run. Initial sampling runs were conducted on the originally selected sites, and identified potential colour hotspots. Following this, hypotheses were developed to explain the observed patterns of DOC occurrence in terms of spatial characteristics. Further sites were then chosen with spatial characteristics selected to provide the best tests of these hypotheses.

Sites were chosen to be accessible from roads wherever possible in order to speed the sampling process. For the majority of sites this was not a problem and others could be reached within one or two kilometres from vehicular access. One potentially attractive site had to be discarded due to problems with access, however this tributary was sampled further downstream.

The catchments of all the sites chosen are shown in Figure 4.2. Table 4.2 records the dates of the sampling runs and on which runs each site was sampled.

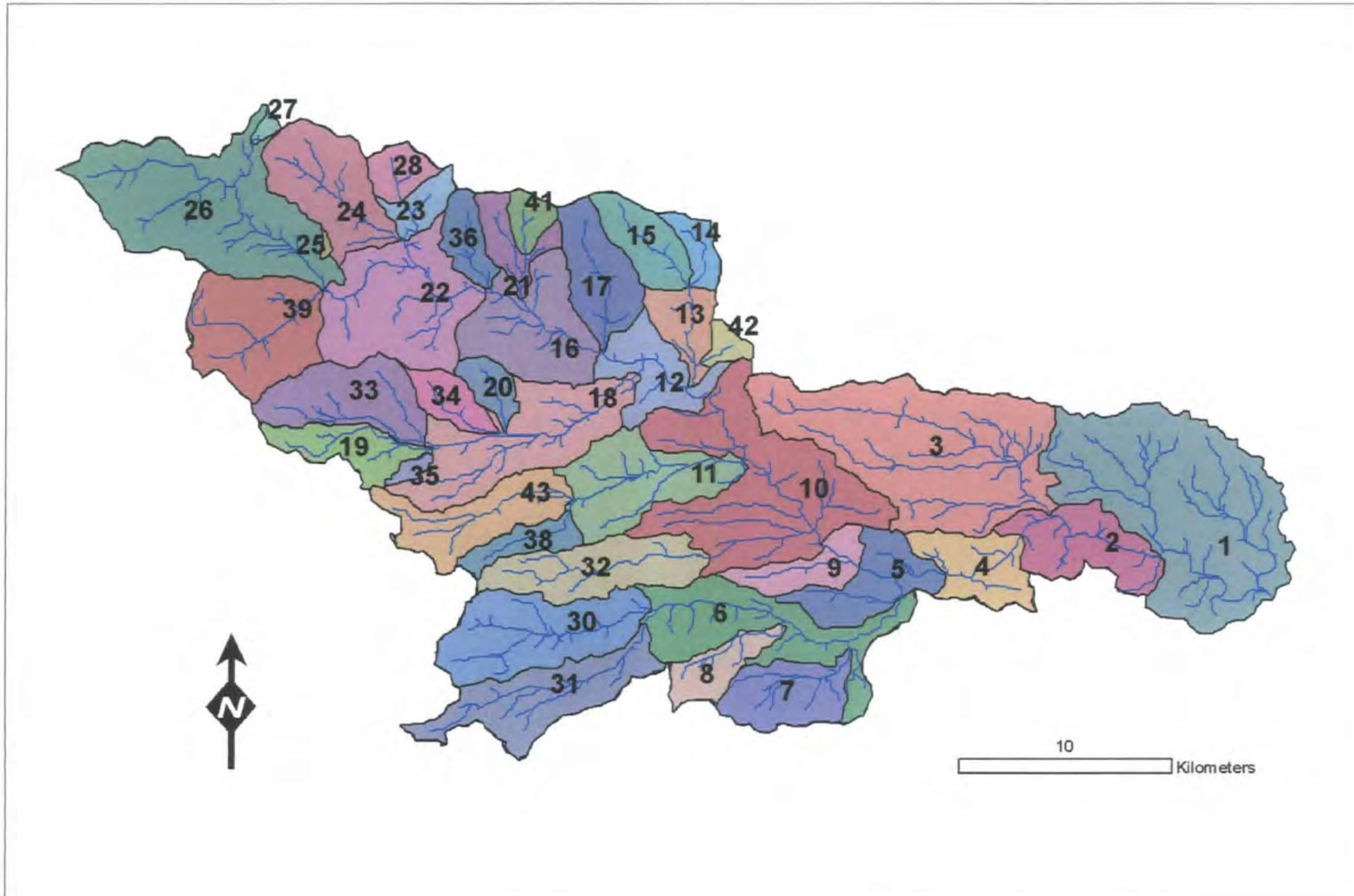


Figure 4.2 All subcatchments surveyed in the study, shown nested. Numbering is that used in Table 4.2

Catchment id	Catchment name	Outlet grid ref	Run 1 04/06/03	Run 2 30/06/03	Run 3 19/11/03	Run 4 09/06/04	Run 5 07/12/04	Run 6 02/03/05	Run 7 28/09/05
1	Tees at Blackwell Bridge	NZ 270125	✓	✓	✓	✓	✓	✓	✓
2	Tees at Piercebridge	NZ 212156	✓	✓	✓				
3	Langley Beck at Gainford	NZ 156176	✓	✓	✓			✓	✓
4	Tees at Winston	NZ 142163	✓	✓	✓				
5	Tees at Whorlton Lido	NZ 107146	✓	✓	✓				
6	Greta at Greta Bridge	NZ 087132	✓	✓	✓	✓	✓	✓	✓
7	Gill Beck	NZ 062105			✓			✓	✓
8	Eller Beck	NZ 031118			✓				
9	Tees at Eggleston Abbey	NZ 065150	✓		✓				✓
10	Tees at Barnard Castle / Startforth	NZ 048162	✓	✓	✓				
11	Balder at Cotherstone	NZ 009200	✓	✓	✓	✓	✓	✓	✓
12	Tees at Eggleston Hall	NY 997233			✓	✓			
13	Eggleston Burn at B6282 road	NY 989240	✓	✓	✓				
14	Little Eggles Hope	NY 992290			✓	✓			
15	Eggleston Burn at Middle End Farm	NY 985288	✓	✓	✓	✓			
16	Tees at Middleton	NY 945253	✓	✓	✓	✓	✓	✓	✓
Cont…									

Catchment id	Catchment name	Outlet grid ref	Run 1 04/06/03	Run 2 30/06/03	Run 3 19/11/03	Run 4 09/06/04	Run 5 07/12/04	Run 6 02/03/05	Run 7 28/09/05
17	Hudeshope Beck at Middleton	NY 946254	✓	✓	✓	✓	✓	✓	✓
18	Lune at B6277 road	NY 960240	✓	✓	✓	✓	✓	✓	✓
19	Lune Head Beck	NY 866206	✓	✓	✓	✓	✓	✓	✓
20	Beck at Wemmergill Hall	NY 900219			✓	✓	✓		
21	Bowlees Beck	NY 907282	✓	✓	✓	✓	✓	✓	✓
22	Tees below High Force	NY 889283	✓	✓	✓				
23	Langdon Beck at Intake Farm	NY 853310	✓	✓	✓	✓		✓	
24	Harwood Beck at Intake Farm	NY 859310	✓	✓	✓	✓		✓	
25	Widdybank site	NY 818304	✓	✓	✓	✓			
26	Tees at Cauldron Snout	NY 814288	✓		✓	✓			
27	Crook Burn at B6277 road	NY 781358	✓	✓	✓	✓			
28	Langdon Beck at weardale road	NY 850330	✓	✓					
29	N/A (could not be accessed)								
30	Greta above Sleightholme confluence	NY 951121				✓	✓	✓	✓
31	Sleightholme Beck	NY 964111				✓	✓	✓	✓
32	Deepdale Beck	NY 991155				✓	✓	✓	✓

Cont...

Catchment id	Catchment name	Outlet grid ref	Run 1 04/06/03	Run 2 30/06/03	Run 3 19/11/03	Run 4 09/06/04	Run 5 07/12/04	Run 6 02/03/05	Run 7 28/09/05
33	Long Grain	NY 867208				✓	✓	✓	✓
34	Hargill Beck	NY 895217				✓	✓		✓
35	Rennygill Sike	NY 863204					✓	✓	✓
36	Etters Gill	NY 893285				✓	✓	✓	✓
37	N/A (could not be accessed)								
38	Hunder Beck	NY 933181				✓	✓		✓
39	Maize Beck	NY 812283				✓			
40	N/A (could not be accessed)	NY 912300				✓			
41	Flushiemere	NY 910302				✓			
42	Blackton Beck	NY 995250				✓			
43	Balder above Blackton reservoir	NY 932182				✓			

Table 4.2 Names, outlet locations, identification numbers, and dates surveyed for all subcatchments

4.3.2 Sampling strategy

Sampling runs were each conducted on a single day and the number of samples taken on each occasion ranged between 18 and 29. On each occasion the first sample collected was from the River Tees above Broken Scar. Subsequent samples were taken by following the most direct route possible between sites up the catchment, and in all cases the samples were all collected within 8 hours. The intention was to conduct the majority of sampling runs at times when there had been at least one week of antecedent dry weather, such that flow was baseflow-dominated. Although higher DOC concentrations may be expected to be linked to storm events, the rapid and flashy response of the catchment and subcatchments meant that there would have been significant variation between the flow conditions under which each individual sample was taken during the day-long sampling period. As it is expected that DOC concentration would vary over the storm hydrograph, this would have caused problems with the comparison of samples for later derivation of colour production models with different samples coming from different points in the hydrograph. However, this aim was not entirely successful due to the unpredictability of weather in the upland regions, a point that is discussed further in the results sections of this chapter.

Where possible, samples were collected by direct immersion of the sample bottle in flowing water in mid-stream and approximately halfway up the water column, in order to ensure a representatively-mixed sample. Where direct access to the stream or river was not possible due to fences or steep banks, a weight-operated remote sampler was used to obtain samples from bridges crossing the water. The remote sampler was equipped with fins to orient it in the direction of water flow. Where used, the sampler was held in place in the water for several seconds in order to ensure that the chamber was thoroughly rinsed through with the local water before release of the weight to capture the sample. In either case the samples were obtained from at least 15cm below the water surface, where the depth of the stream was sufficient to allow this. Samples were collected into one litre PVC wide-mouthed sample bottles, which had been acid washed and pre-rinsed with sample water. These were closed with no headspace, stored upright in the dark and, once returned to the laboratory, refrigerated prior to analysis within 48 hours.

4.3.3 Sample analysis

4.3.3.1 DOC concentration

Samples were analysed for DOC concentration on the day following collection. DOC was measured directly on all samples with the exception of the 7th December 2004 run. DOC analysis was conducted following the method of Bartlett and Ross (1988). Absorbance measurements were conducted at 495nm using a spectrophotometer (Camspec Ltd M100). Each sample was placed in individual polystyrene cuvettes and the blank absorbance was first measured for each cuvette filled with distilled water. Organic carbon standards for the calibration were mixed from a serial dilution of a 100ppm oxalic acid solution.

4.3.3.2 Sample absorbance

Samples were measured for absorbance at 400nm using individual polystyrene cuvettes in the spectrophotometer. Absorbance was also measured at 465nm and 665nm as part of a separate study. Data for absorbance at 400nm and DOC concentration were used in the DOC calibration experiment for the sampling programme detailed in chapter 2, and 400nm absorbance data were used to derive DOC concentrations for the one set of samples where direct colorimetric analysis did not take place. Details of the calibration relationship derived and used are given in section 2.7.3.

4.3.3.3 Metal ion content

Samples were analysed for several base metal cations commonly found in streamwaters. Analysis was conducted using an ICP-OES technique (Inductively Coupled Plasma – Optical Emission Spectroscopy); results and analysis of these data are presented in chapter 5.

4.4 GIS Mapping and modelling

4.4.1 Datasets obtained

4.4.1.1 DTM

Digital terrain model (DTM) data were extracted for the area of the catchment from the Ordnance Survey 50m horizontal resolution nationwide DTM. The data was obtained from the EDINA Digimap service and imported into Esri Arcmap 9.0 using the supplied ESRI Map Manager tool. For checking the derived stream network in certain areas, portions of the 10m resolution DTM were also extracted. The 50m DTM was filled to remove sinks and used in the terrain analysis.

4.4.1.2 Soil cover – Land Cover Map

Data from the full-resolution Land Cover Map 1990 (Fuller et al, 1994) was provided for the area of the catchment by CEH Data Services (http://science.ceh.ac.uk/data/lcm/index.htm)

The Land Cover Map classifies land cover into 25 different classes at a 25m resolution. The dataset was produced using a semi-automatic classification of Landsat Thematic Mapper data (Fuller et al 1994) and is therefore primarily a map of soil cover type, especially vegetation, rather than of underlying soil types. Once imported into the GIS, an estimate of peat cover was produced by selecting those areas of the LCM data with vegetation types that are most commonly underlain by peat soils. The LCM classes selected are shown in Table 4.3:

Class number	*Description*	*Notes*
5	Grass heath	Largely lowland grass but distinguished by acid-loving types
9	Moorland grass	Grass moorland or upland grass heaths, may include sparse dwarf shrubs such as heather
8	Rough / Marsh grass	Uncropped and unmanaged grasses
10	Open shrub moor	Heather moorland largely grazed or burnt leading to non-dense heather
11	Dense shrub moor	Including heather moorland and some grasses
17	Upland bog	With standing water, may not include heather-dominated regions

Table 4.3 LCM(1990) classes selected, from Fuller et al (1994)

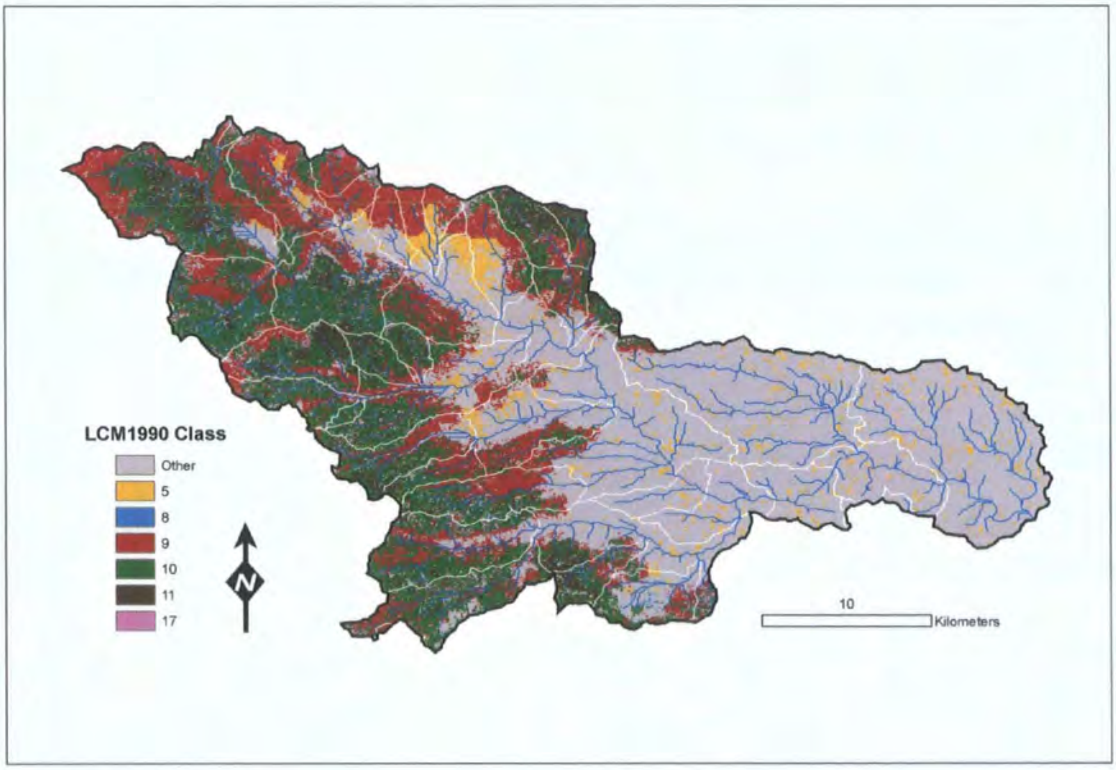


Figure 4.3 Areas selected from the LCM(1990) map

4.4.1.3 Soil cover – Hydrology of Soil Types

Because the LCM1990 dataset primarily provides information on vegetation cover, from which soil type can be implied, rather than soil type directly, data was also obtained from the Hydrology of Soil Types (HOST) national dataset

(Boorman et al, 1995). This dataset takes into account physical soil type and also the predicted hydrological response of the soil based on factors such as the underlying substrate. The HOST dataset therefore provides a more direct indication of peat cover than does the LCM data. The data was imported into the GIS in the "percentage type cover" format whereby each cell is allocated a value for each HOST class for the percentage of that cell covered by that class. Once imported, an estimate of peat cover was produced by selecting as peat those cells which had a dominant cover (i.e. greater than 50% cover) of peat type soils. In the HOST classification the peat soils are classes

HOST class number	*Description*
11	**Drained peats with aquifer connectivity at < 2m**
12	**Undrained peats with aquifer connectivity at < 2m**
15	**Peats with aquifer connectivity at > 2m**
26	**Peat over slowly permeable hydrogeological types**
27	**Peat over impermeable hydrogeological types**
28	**Eroded peats**
29	**Raw peat**

Table 4.4 Classes selected from the HOST dataset, from Boorman et al (1995)

Of these only classes 12, 15, 26 and 29 were represented within the catchment and in practice most peat areas in the catchment are allocated to classes 26 and 29.

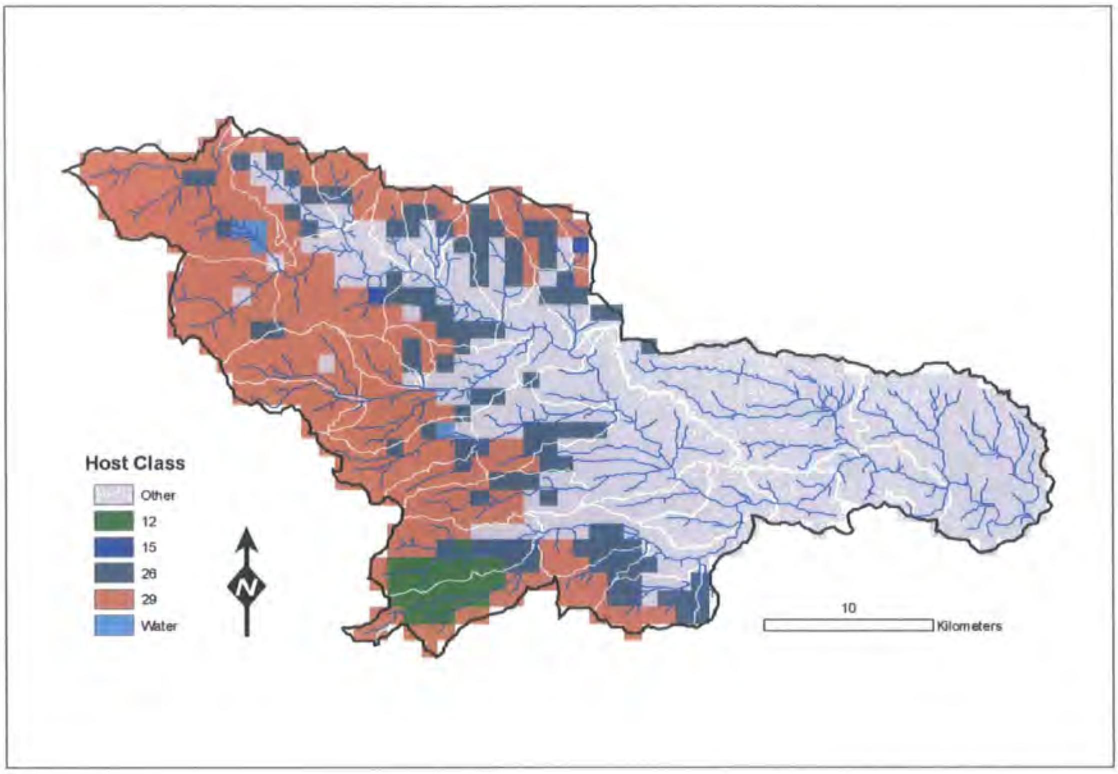


Figure 4.4 Areas selected from the HOST dataset - note 1km resolution.

The HOST dataset provides a more specific identification of peat areas than does the LCM dataset. However the HOST dataset was only available at a 1km resolution, which for some of the smaller catchments in this study represented a significant degradation in accuracy as a small catchment may be represented by only one or two HOST cells, in which case peat cover can only be recorded as 0%, 50% or 100%. Aitkenhead et al (1999) used three different measures of soil carbon content of which one, sourced from the Department of the Environment (DoE), was based on the dominant cover type in 1km cells, similar to the HOST identification of peat described above. They found that that this measure did not act as a significant predictor of DOC concentration whereas the other two higher-resolution measures did; this was explained by the lower spatial resolution of the DoE dataset (Aitkenhead et al, 1999). The DoE dataset has been found to be a significant predictor of DOC export in a study involving larger catchments (Hope et al, 1997a), where it would be expected that the inaccuracy introduced by this low resolution would be less significant, but the catchments studied by Aitkenhead et al (1999) were of similar size ranges to those in this study and their finding is likely to be the more relevant to this study.

Therefore the higher resolution LCM1990 dataset was chosen as the preferred source for percentage peat cover data. In any case, total area selected as peat was very similar from both datasets – the largest catchment in this study, Broken Scar, was estimated as 51.7% peat cover from the LCM1990 dataset and 51.2% from the HOST dataset, and therefore this use of LCM1990 data was judged appropriate.

4.4.1.4 Land cover – Landsat Thematic Mapper

The Thematic Mapper is an electromagnetic remote sensing device carried by the Landsat 5 and Landsat 7 satellites. Data is recorded separately over seven portions or "bands" of the electromagnetic spectrum, ranging from blue visible light to thermal infrared. A detailed discussion of the scope and use of the different LTM bands is beyond the scope of this study. Briefly however, the thematic mapper records brightness values – which when normalised to the overall scene brightness correspond to spectral reflectance – for each of the discrete wavelength bands. Different land characteristics produce distinctive reflectances at specific wavelengths and so different LTM bands are of use in identifying different types of land cover. For example, the red and near-infrared bands are excellent for distinguishing vegetation cover. Vegetation absorbs a large proportion of blue and red light, meaning its reflectance in these bands is low, whilst it reflects a large proportion of near-infrared light. Each of these bands is therefore a useful indicator of vegetation cover and taken together the bands can provide an indication of vegetation type and condition – as near-infrared reflectance for example changes with moisture content. Whilst this concept of combining information from several LTM bands has been extended to produce specific indices, for example the Tasseled Cap Wetness index (Crist and Cicone, 1984; Crist, 1985), such consideration of remote sensing techniques was considered beyond the scope of this study, and the bands have been considered only separately.

Visual display, for example on a computer monitor, relies on each pixel being allocated a value for each of red, green, and blue. If the values allocated for each pixel are those from the red, green, and blue bands of the Landsat image, then the image produced will approximate that which would be observed by the naked eye. However, other bands could be "mapped" to the red, green, or blue display values and this is the basis for false-colour images which may be produced to emphasise different characteristics. For example, assigning the red display channel to the LTM band 4 (near-infrared), green to LTM band 3 (red) and blue to LTM band 2 (green) results in a false-colour image that is excellent for distinguishing vegetation type visually.

Brightness values for each pixel in each band are recorded in an 8 bit format; there are 256 possible brightness values. In many scenes the full gamut is not utilised, for instance a scene may only contain pixel values in the range 100 – 150 for a given band. The data can therefore be stretched using image processing techniques to improve the contrast. Stretches may be a simple minimum-maximum, whereby the pixel values are normalised to a maximum of 255 and minimum of 0, or may be based on other manipulations of the brightness histogram.

Since such alternative histogram processing methods do not necessarily represent linear functions across the range of input pixel values, different results can be obtained depending on what image processing is applied to the raw data. Therefore Landsat Thematic Mapper data was obtained for the study catchment from three separate sources. Firstly, data was obtained from the Landmap service (http://landmap.ac.uk) that included six wavelength bands of the seven available in the original data. The data in this set was fully orthorectified and projected into the British national grid, but the pixel brightness values are unstretched as supplied, resulting in an image that is visually low in contrast. Secondly, a processed version was obtained from the NASA Geocover dataset (https://zulu.ssc.nasa.gov/mrsid/mrsid.pl). This set is from the Landsat 7 Thematic Mapper and takes the form of a composite image formed from bands 7, 4 and 2 in the red, green and blue channels respectively. Image histograms were stretched in order to match adjacent scenes in the resulting seamless dataset – therefore the actual stretch applied was not the same for each scene and is not published. Finally a pre-processed version of the Landsat Thematic Mapper data was extracted from the free "Window on the UK" CDROM distributed by the BNSC (http://www.bnsc.org/wouk/wouk1.htm).

This dataset is also supplied as a set of RGB colour composite images in a standard raster format. The red, green and blue channels of the composite images supplied on the WOUK CD are produced from bands 3, 2, and 1 of the Landsat 5 thematic mapper, which approximately correspond to visible red, green, and blue light respectively, so that the composite RGB image is close to being a true "visible" colour image. The images are processed for brightness and contrast but the actual stretch applied to each image is not published. However the dataset is readily available for the entire UK, enabling its use in other areas without this knowledge.

The Landcover and WOUK datasets are supplied as composite RGB images, but the red, green and blue channels of the composite image datasets can be separated by image processing software to retrieve the separate thematic mapper bands: for instance the red channel of the WOUK image represents band 3 of the LTM data. Therefore the red channel of the image, corresponding to the red band 3 in the LTM data, was extracted and mean brightness values for this band were calculated for each study catchment. From the Geocover dataset, mean values were calculated from each TM band for each study catchment. From the multiband data obtained from Landmap, TM bands 3 and 4 were extracted, and since the data was supplied unstretched, the images were also processed by a histogram equalisation method to increase contrast. Mean values were calculated for each band and catchment for both the processed and unprocessed images.

4.4.2 Derived datasets

4.4.2.1 Stream network

The stream network was derived from the DTM in Esri ArcMap 9.0 using the hydrology modelling tools. The process of stream network derivation has three stages. First, any sinks in the terrain model are identified and filled. Sinks in the DTM for such a largely steep catchment are rare and due to the high quality of the Ordnance Survey DTM few were found. However where they do exist they must be filled so that the flow direction can be correctly calculated for all cells. The standard fill method is to raise the height of the sink cell(s) until the sink spills.

Secondly, from this filled DTM a flow direction grid is calculated: the height of each cell is compared to that of each of the surrounding 8 cells to calculate the downslope direction, and this direction value is then allocated to the central cell. Thirdly, this information from each cell is combined to create a total "flow accumulation" grid where each cell is allocated a value representing the number of other cells which flow into it. This flow accumulation grid can be simply converted to a stream network by selecting an appropriate flow accumulation threshold value. For instance, all cells with greater than a certain number of cells flowing into them may be represented as a stream. The appropriate selection of this threshold value has been discussed in Tarboton et al (1991); for this study a value of 40 cells was used as this was found to give the best match of the derived stream network to the streams represented on the highest resolution ordnance survey data available, the 1:10000 scale mapping. 40 cells represents a minimum stream catchment area of $0.1km^2$.

The derived stream network was visually examined to compare with the network recorded on Ordnance Survey 1:10000 scale mapping. The only place where the derived network was found to inaccurately represent the real-world streams was at Baydale Beck, which joins the Tees immediately above the Broken Scar treatment works at NY253140. Baydale beck divides further upstream at NY260156 into Cockerton Beck (which continues out of the catchment) and this branch of Baydale Beck which joins the Tees. Therefore the $24km^2$ catchment of Baydale Beck should be included within the catchment of the Tees at Broken Scar. However the derived stream network does not map this divide at NY260156, showing only Cockerton Beck and therefore not including the catchment of Baydale Beck within the Broken Scar catchment. The details of this subcatchment were therefore manually added to the derived catchment details.

4.4.2.2 Stream characteristics

Strahler stream order and Shreve magnitude were calculated for all links on the stream network and extracted for each sampled catchment point and for each link on the main branch of the Tees. This process is automated within ArcMap. Whilst the derived values are entirely dependent on the detail of the stream network used as input (and therefore how small and numerous are the first order streams), the stream network derived with a 0.1km^2 minimum catchment size was well matched to the stream network represented on large-scale Ordnance Survey mapping. Shreve magnitude of a point on a river represents the total number of first-order streams within the catchment of that point. Figure 4.5 provides an illustration of the relative size of the catchment of the Tees and several major tributaries, compared to the Shreve magnitude. All of these except Summerhouse Beck were sampled in this study and it can be seen that these are the key tributaries to the river in terms of overall drainage input. Largely flat catchments such as the Lune and Langley Beck, while otherwise different in character, can be seen to have a particularly high Shreve magnitude relative to their area.

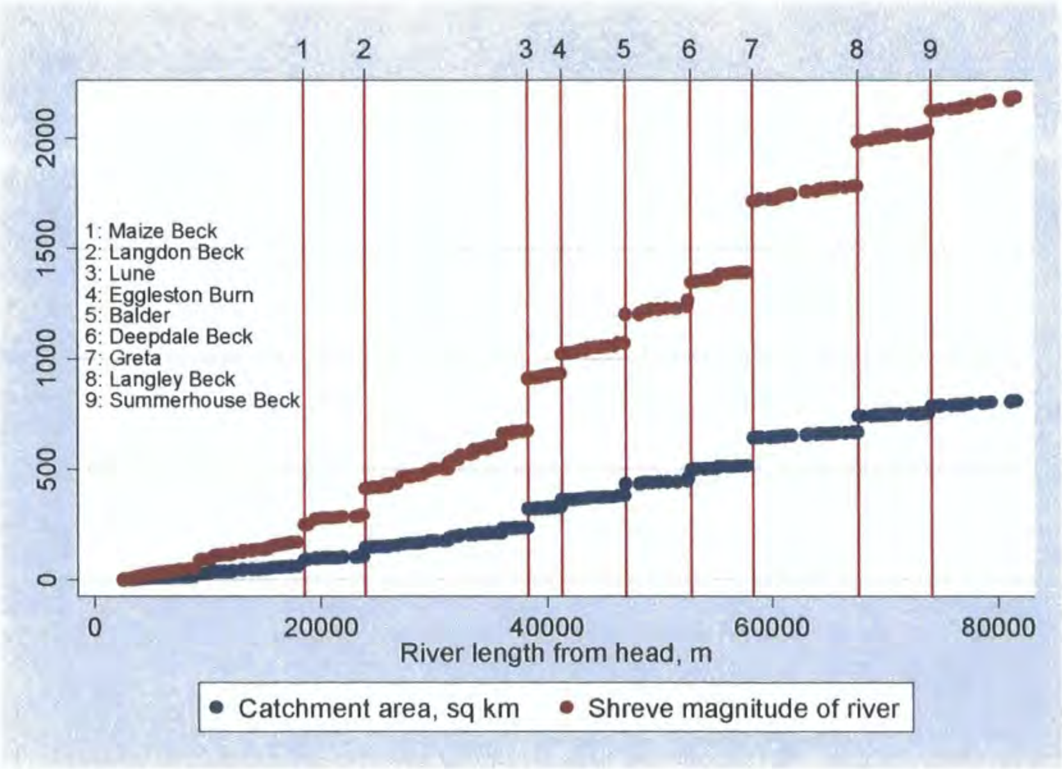


Figure 4.5 Shreve magnitude of the River Tees and the effective catchment area plotted against the flow length from the source, showing the contribution of the major tributaries

Total stream length within each catchment was derived by intersecting the stream network with the catchment outlines and summing the stream segment lengths within each catchment. Maximum flowpath length was calculated to each catchment outlet using the FlowPath tool in ArcMap. Average main stream gradient was calculated from the maximum flowpath length and the elevation range within the catchment. Stream drainage density was calculated from the total stream length within the catchment and the catchment area, and expressed as km stream channel per km^2 of catchment area.

4.4.2.3 Slope and aspect

Slope was derived from the DTM by simply comparing the height of each cell with that of the surrounding 8 cells. Each cell was thus allocated a single "slope" value in degrees, which enabled the calculation of statistics such as average and maximum slope for the catchments. Aspect was expressed in terms of degrees variation from north.

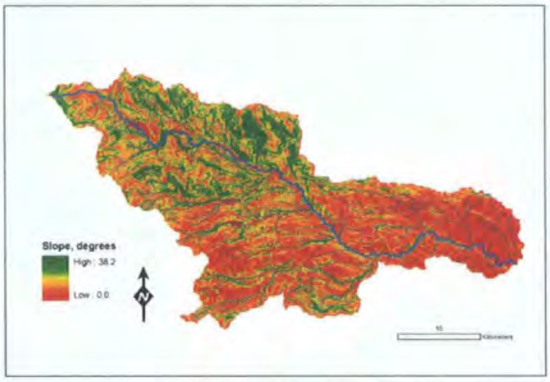


Figure 4.6 Slope in degrees

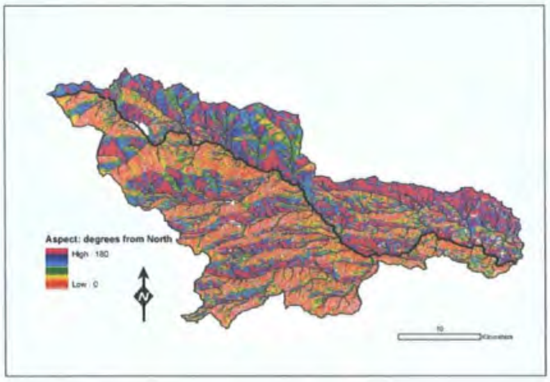


Figure 4.7 Aspect expressed as degrees variation from North

4.4.3 Land Use data

4.4.3.1 Gripped area

The areas of the catchment which have been artificially drained, or gripped, were delineated manually from aerial photography. Access was provided by English Nature to aerial photography from the getmapping.com Millennium Map project (http://www.getmapping.com). This photography was flown in 1999 and has a 25cm pixel resolution or better. At the time of writing, examples of the same photography dataset used can be accessed via http://www.multimap.com and http://local.live.com. Photography is orthorectified and referenced with the OSGB grid to correspond with Ordnance Survey mapping.

Photography for the entire area of the Broken Scar catchment that has peat cover was imported into the MapInfo GIS software, and examined manually on screen. The straight and generally parallel pattern of drains in drained areas is distinctive and was found to be easily distinguished from natural drainage on screen. Areas with this pattern of peatland drains could be clearly identified and were outlined with a polygon overlay on screen in MapInfo. The resulting polygons were then imported into the ESRI ArcMap GIS.

Clearly this method produces a qualitative estimate of drained area with no attention paid either to density of drainage, or to age of drains. To produce such a detailed dataset would require an extremely large scale field survey that was beyond the scope of this project. However this estimate was sufficient for the purposes of this study and the production of a generalised predictive model of DOC export.

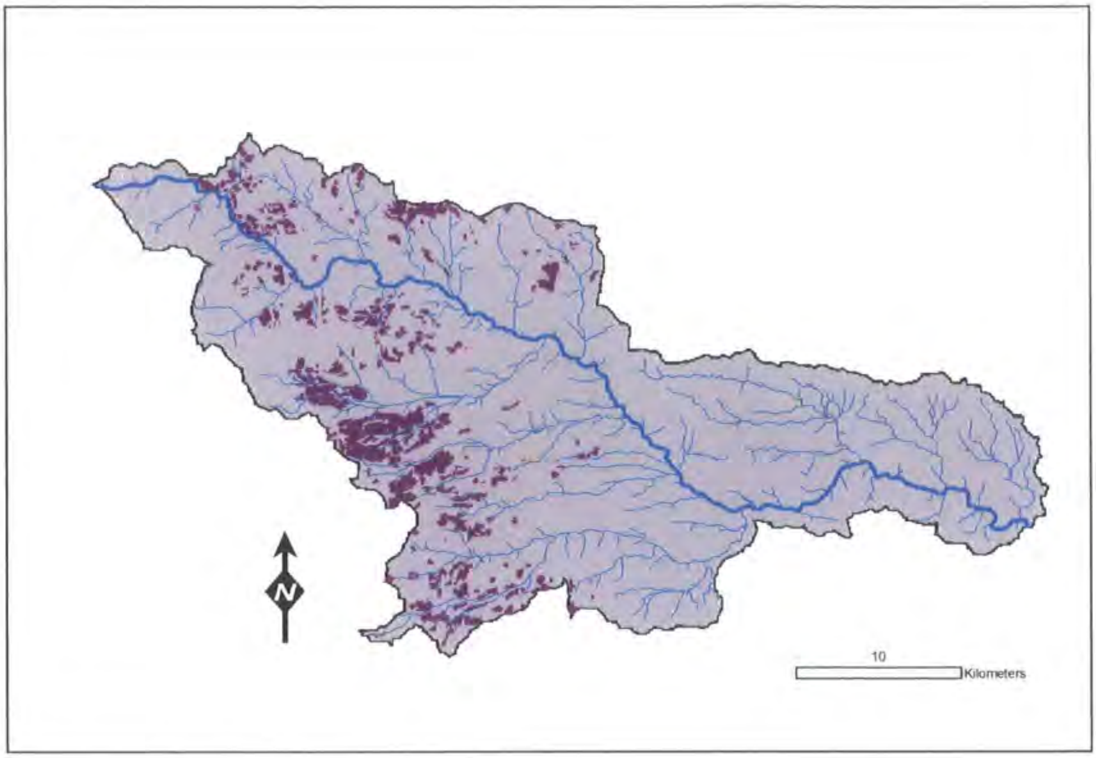


Figure 4.8 Areas selected as gripped from aerial photography

4.4.3.2 Burnt Area

The same aerial photography and software was also used to derive a map of burnt area within the catchment. The characteristic patchwork pattern of heather burning, caused by the burning taking place on small areas at a time on a rotating cycle basis, could again be readily distinguished in the aerial photography. A polygon overlay was again created to cover the identified areas and imported into the ArcMap GIS.

Identification of burnt areas was possibly even more subjective than that of drained areas. Burning takes place only over small areas in any one year and the recovery of the heather, and thus its visual appearance in aerial photography and subsequent identification as a burnt area, will depend on many variables such as the weather conditions since burning and the altitude and exposure of the heather. Nevertheless, it was considered that the derived dataset was a useful estimate of those areas which are subject to a regular rotating burning programme over recent decades.

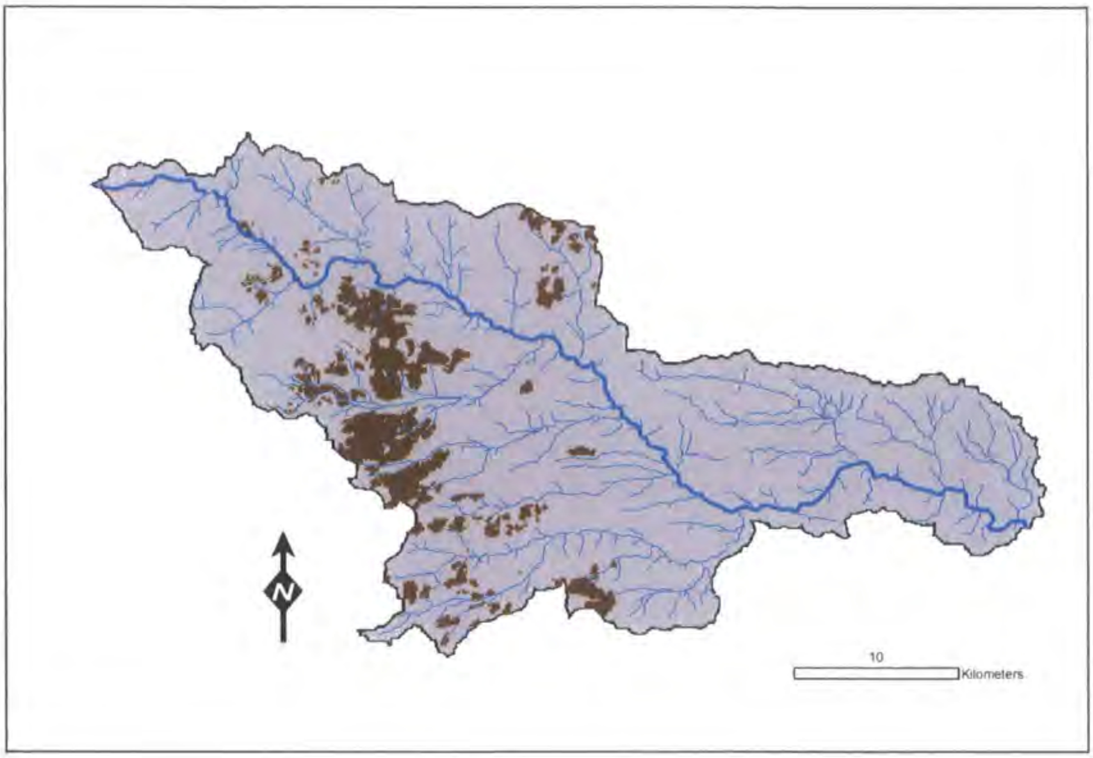


Figure 4.9 Areas selected as burnt from aerial photography

4.4.3.3 Grazing Intensity

It was considered that some measure of grazing intensity should be made available as input to the modelling. Since 1866, an annual agricultural census has been conducted by DEFRA (Department for Environment, Food, and Rural Affairs), previously known as MAFF (Ministry for Agriculture, Fisheries, and Food), or the equivalent government departments of the time (DEFRA, 2006). The census was until 1995 completed by all farms. The data gathered by this census have varied over time but have always included a measure of land area used for crops, for pasture, and as rough grazing (including moorland), in addition to numbers of sheep, cattle, and other livestock. Theoretically these data enable an estimate to be made of grazing intensity at a resolution of the size of a farm. However, the data were only released to the public aggregated to whole parishes, to comply with requirements of the Data Protection Act and equivalent legislation.

More recent census results are released aggregated to wards rather than parishes, equivalent to the NUTS-5 or LAU2 classification of land unit areas

(ONS, 2004). In practice, in rural areas such as the Broken Scar catchment this means aggregation to coarser units than parishes. Additionally the census is no longer completed by every farm in every year but is instead issued to a selection of farms each year and the results interpolated to produce total estimates (with the exception of every tenth year where a complete census is still conducted). While this interpolation may be largely accurate over larger aggregation units in more densely farmed areas, it inevitably reduces accuracy over the earlier surveys in rural areas of few, physically large, farms and parishes.

The census summaries for years prior to the end of complete surveys are held at the Public Records Office (PRO), Kew, with one record existing for each parish for each year. Parish boundaries, which have changed at intervals, were obtained for each relevant year from Edina Digimap and imported into the ESRI ArcMap document, to identify the parish records required. These records were then obtained from the PRO for every other year from 1960 – 1988 (the most recent available). The data were electronically entered and tabulated in a format that could be imported into the GIS. It is believed that this is the first time that any part of the agricultural census data from these earlier dates has been digitised.

4.4.4 Catchment Characterisation

4.4.4.1 Catchment Delineation

Catchments were outlined in the GIS using the same Hydrology Toolset described in section 4.4.2.1. The catchment outlet locations as measured using a differential-corrected GPS device (Garmin Etrex Summit) were imported into the GIS and were used as points from which to define a catchment. These actual sampling points were all found to fall upon streams predicted by the stream network creation process, adding confidence to the accuracy of the model. To delineate a catchment, the outlet point, which should be on a modelled stream, is selected. The catchment tool then searches the flow direction grid for all the cells from which any runoff that forms will eventually pass through the selected point. The area covered by the cells thus selected represents the catchment of that point. The catchment generation algorithm proved quite sensitive to the exact location of the outlet point chosen relative to the flow accumulation grid, so the outlet points were first snapped to the highest flow accumulation point within a 100m radius, and all generated catchments were examined manually to check that they were realistic. Adjacent catchments were also examined to ensure that they had a common boundary without overlap. The raster layer representing all the nested catchments was then converted to a polygon layer containing a separate feature for each entire catchment.

4.4.4.2 Statistical representation of catchments

The aim of this part of the study is to develop a statistical relationship between the characteristics of the catchments as represented in the datasets discussed above, and the DOC concentration. To derive the variables for each catchment, the datasets discussed above were analysed on a catchment by catchment basis. For raster-based data layers, this was achieved using the Zonal Statistics tool within Spatial Analyst in ArcMap. The polygon layer of the catchments was used as the zone definitions for the Zonal Statistics tool run on each of the raster datasets in turn. This enabled the rapid production of comprehensive statistics such as, for instance, average slope, maximum slope, total relief, or percentage peat cover, for each catchment. Statistics relating to the stream characteristics were produced by intersecting the catchment polygons with the relevant vector network layers. The output statistics from each technique were readily exported in a form that could be loaded into a spreadsheet or statistics package for analysis and as such the process was much faster and more accurate than manual production of such statistics undertaken in previous studies.

From the datasets described above, thirty-one spatial characteristics included in the study by Mitchell and McDonald (1995) were derived (all the characteristics from the study except number of springs, denoted Spr in that study). A number of other variables were also calculated; 57 in total. All the variables studied are tabulated in Table 4.5 - Table 4.8.

Land use and cover datasets were recorded as overall area represented within the catchment, and the fraction of the total catchment area, for example burnt area and burnt fraction for the burning dataset. Fraction peat ungripped records the fraction of total peat covered catchment area (according to the LCM dataset) that is not gripped. Slope and elevation were recorded as maximum, minimum, range, and standard deviation of values observed within each catchment. Reflectance values for the various Landsat datasets were recorded as mean values for each catchment. A3deg and A5deg record the total area with slope of less than 3 and 5 degrees respectively and %A3deg and %A5deg are the fraction of total catchment area represented by these. CLA3deg and CLA5deg are the total channel lengths in these areas and TCLA3deg and TCLA5deg are the fractions of the catchment total channel length that is in these areas.

Variable name	Source (*)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Area km^2	Yes	839.8	757.4	72.3	664.4	648.9	118.7	17.1	9.5	512.8	501.9	54.9	364.8	31.4	5.5	12.7	214.0	17.5	85.9	14.2	5.9
Elevation min m	Yes	36	54	71	75	97	124	193	232	118	128	160	181	192	330	328	215	218	212	354	317
Elevation max m	Yes	889	887	445	887	887	589	544	514	887	887	561	887	652	583	652	887	671	787	743	618
Elevation range m	Yes	853	833	374	812	790	465	351	282	769	759	401	706	460	253	324	672	453	575	389	301
Elevation mean m	No	356	384	181	415	422	377	372	394	440	445	364	495	440	463	500	531	461	474	515	494
Elevation std. dev.	No	178	163	63	148	143	89	85	68	145	142	76	125	91	48	72	114	102	117	71	60
Slope min deg	No	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Slope max deg	No	38.2	38.2	22.7	38.2	38.2	28.3	17.3	21.5	38.2	38.2	23.8	38.2	30.7	17.9	25.1	38.2	26.5	29.2	21.4	14.6
Slope range	No	38.2	38.2	22.7	38.2	38.2	28.3	17.3	21.5	38.2	38.2	23.8	38.2	30.7	17.9	25.1	38.2	26.5	29.2	21.4	14.6
Slope mean deg	No	4.3	4.6	3.0	4.8	4.9	3.7	5.1	3.8	5.2	5.2	3.9	5.9	6.8	5.8	7.2	5.7	8.6	5.4	4.7	5.9
Slope st. dev. Deg	No	3.5	3.5	2.4	3.5	3.5	3.0	3.1	2.9	3.6	3.6	2.8	3.6	3.8	3.1	3.9	3.5	4.0	3.6	2.9	2.7
Mean aspect	Yes	91.6	89.0	106.9	87.5	87.4	68.3	46.4	42.8	91.9	92.2	75.8	94.6	108.5	114.1	103.2	88.9	116.9	98.5	73.4	116
A3deg km^2	Yes	378.5	304.2	45.1	242.5	230.9	61.0	5.0	4.7	158.7	151.5	24.8	78.4	4.1	0.9	1.6	43.6	1.3	24.7	4.5	0.9
%A3deg	Yes	45.1	40.2	62.3	36.5	35.6	51.4	29.2	49.0	30.9	30.2	45.1	21.5	12.9	15.8	12.2	20.4	7.3	28.7	31.6	15.4
A5deg km^2	Yes	567.5	487.5	61.4	407.3	393.7	89.9	9.7	7.2	288.5	278.7	40.9	171.4	11.5	2.7	4.3	100.9	3.4	47.0	9.0	2.4
%A5deg	Yes	67.6	64.4	84.8	61.3	60.7	75.7	56.9	75.6	56.3	55.5	74.4	47.0	36.7	47.3	32.9	47.1	19.4	54.6	63.3	40.3
Basin length km	Yes	61	55	15	49	46	24	6	6	43	40	18	33	11	4	6	27	7	16	8	4
Elongation	Yes	1.0	1.0	1.1	1.1	1.1	0.9	1.3	1.0	1.1	1.1	0.8	1.2	1.1	1.2	1.1	1.1	1.2	1.2	0.9	1.3
Perimeter km	Yes	192	181	45	164	153	72	19	17	123	121	46	97	30	12	15	78	19	48	21	11
Crenulation	Yes	44.0	43.2	28.6	40.6	35.8	44.2	21.4	29.6	29.4	29.1	39.1	25.9	27.8	25.0	18.8	28.6	21.3	26.5	30.8	21.2
Geometry number	Yes	359	325	30	286	279	51	7	4	220	216	24	157	17	4	7	89	9	37	6	3
Relief ratio	Yes	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.1
Relative relief	Yes	4.37	4.19	1.59	4.05	4.25	1.64	0.89	0.57	4.17	4.15	1.18	3.75	1.06	0.47	0.82	2.74	0.91	1.80	0.68	0.53
CLA3deg km	Yes	1080	885	134	712	685	162	15	14	494	474	70	279	8	1	3	166	2	81	17	1
%TCLA3deg	Yes	54.9	50.2	77.4	46.0	45.3	58.7	33.7	52.1	41.4	40.7	56.0	32.8	14.9	16.7	12.1	32.2	5.7	40.7	48.6	12.5
CLA5deg km	Yes	1498	1297	161	1093	1063	226	28	21	799	776	101	513	22	4	6	317	6	138	28	5
%TCLA5deg	Yes	76.1	73.5	93.0	70.7	70.3	81.7	63.9	82.8	67.0	66.5	80.7	60.5	38.1	54.1	26.6	61.6	17.6	69.2	79.9	40.1

Table 4.5 Derived statistics (a) for catchments 1-20. *=included by Mitchell & McDonald(1995)

Variable name	Source (*)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1st orders	Yes	2254	2032	203	1774	1729	300	47	22	1386	1355	128	1035	88	12	36	613	50	231	31	21
2nd orders	Yes	492	443	43	387	376	64	9	7	305	303	32	231	19	2	8	136	11	55	9	6
3rd orders	Yes	106	92	8	82	80	15	3	3	63	62	6	47	4	1	2	32	1	9	2	1
Strahler Order	No	6	6	5	6	6	5	4	4	6	6	4	6	4	3	3	6	3	5	4	3
Shreve Magnitude	No	2184	2027	203	1774	1729	297	47	21	1386	1355	128	1035	88	12	36	613	50	231	31	21
Max Stream length, km	Yes	81.6	73.5	19.6	65.3	60.5	30.7	8.9	8.9	55.7	53.6	20.9	42.6	13.0	5.6	7.4	35.8	8.8	22.0	10.4	5.2
Main stream gradient %	Yes	1.0	1.1	1.9	1.2	1.3	1.5	3.9	3.2	1.4	1.4	1.9	1.7	3.5	4.5	4.4	1.9	5.1	2.6	3.7	5.8
Total channel length km	Yes	1967	1764	173	1546	1512	277	44	26	1193	1167	125	848	57	7	22	515	34	200	34	12
Stream density km / km^2	Yes	2.3	2.3	2.4	2.3	2.3	2.3	2.6	2.7	2.3	2.3	2.3	2.3	1.8	1.3	1.8	2.4	1.9	2.3	2.4	2.0
Stream frequency	Yes	5.4	5.4	5.6	5.3	5.3	5.0	5.5	4.5	5.4	5.4	4.6	5.7	5.6	4.2	5.6	5.7	5.7	5.4	4.3	7.0
Drainage intensity	Yes	2.3	2.3	2.3	2.3	2.3	2.2	2.1	1.7	2.3	2.3	2.0	2.4	3.1	3.3	3.2	2.4	2.9	2.3	1.8	3.5
Bifurcation ratio	Yes	4.6	4.6	4.7	4.6	4.6	4.7	5.2	3.1	4.5	4.5	4.0	4.5	4.6	6.0	4.5	4.5	4.5	4.2	3.4	3.5
Length overland flow	No	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.2	0.3	0.2	0.2	0.3
Burnt fraction	No	0.08	0.09	0.00	0.11	0.11	0.10	0.03	0.35	0.11	0.12	0.18	0.13	0.16	0.22	0.18	0.06	0.03	0.30	0.27	0.44
Burnt area km^2	No	70.7	70.6	0.0	70.5	70.5	11.6	0.6	3.3	58.9	58.9	9.7	45.7	4.9	1.2	2.3	13.7	0.5	26.1	3.8	2.6
Gripped fraction	No	0.07	0.08	0.00	0.09	0.09	0.08	0.00	0.07	0.10	0.10	0.17	0.10	0.06	0.05	0.11	0.09	0.03	0.20	0.32	0.11
Gripped area km^2	No	60.4	60.3	0.0	60.3	60.3	10.0	0.0	0.7	50.4	50.4	9.3	38.2	2.0	0.3	1.3	18.9	0.5	16.8	4.5	0.6
Fraction peat cover	No	0.52	0.57	0.07	0.64	0.65	0.63	0.47	0.84	0.67	0.69	0.65	0.77	0.85	0.95	0.92	0.81	0.67	0.79	0.91	0.92
Peat area, km^2	No	434.2	428.7	5.0	422.6	421.8	75.3	8.1	8.1	345.5	345.0	36.0	281.9	26.7	5.3	11.7	172.9	11.6	68.3	12.9	5.4
Fraction peat ungripped	No	0.86	0.86	1.00	0.86	0.86	0.87	1.00	0.91	0.85	0.85	0.74	0.86	0.93	0.95	0.88	0.89	0.96	0.75	0.65	0.88
Sheep/sqKm 88 mean	No	308	311	525	289	286	341	193	260	270	269	375	235	300	301	291	265	293	128	165	137
Sheep/sqKm 80 mean	No	217	221	317	213	209	292	133	214	190	189	144	178	236	237	227	190	227	124	156	138
LTM_{WOUK3}	No	85.1	79.9	94.7	76.6	75.3	72.6	65.5	68.2	74.8	74.6	72.6	74.9	67.7	63.6	64.8	77.6	79.7	70.2	68.9	65.4
LTM_{band3}	No	28.9	28.9	26.9	29.4	27.9	27.3	29.7	28.9	27.2	26.7	28.3	26.7	29.5	27.8	29.0	31.1	31.7	29.6	31.4	28.6
LTM_{band4}	No	102.2	100.4	77.1	105.4	86.7	90.7	129.0	119.8	84.4	78.9	107.9	80.0	126.2	97.3	118.1	146.0	159.1	123.6	158.1	118.4
$LTM_{band3eq}$	No	93.6	94.1	102.5	98.2	100.2	85.7	68.9	58.2	98.3	96.9	90.7	97.4	70.0	50.1	54.1	85.2	78.1	83.9	57.3	55.4
$LTM_{band4eq}$	No	197.5	202.3	210.2	218.7	214.7	213.0	206.5	210.1	180.9	92.6	79.4	173.3	81.6	121.7	197.2	175.2	95.6	77.8	69.7	79.8
$LTM_{lcband7}$	No	140.3	140.3	114.1	139.6	118.4	97.0	79.0	106.6	103.5	96.0	97.6	95.9	127.7	127.0	127.0	127.7	138.4	103.7	132.8	117.7
$LTM_{lcband4}$	No	127.9	126.8	167.7	139.0	153.3	159.8	136.5	116.5	170.0	175.2	166.0	171.6	129.1	93.0	96.7	149.9	140.5	140.5	98.5	92.2
$LTM_{lcband2}$	No	114.1	116.7	99.0	118.8	101.5	81.1	68.7	60.4	96.9	87.8	86.2	86.6	78.2	58.5	62.2	100.2	97.6	81.1	68.2	51.4

Table 4.6 Derived statistics (b) for catchments 1 – 20. *=included by Mitchell & McDonald(1995)

Variable name	Source (*)	21	22	23	24	25	26	27	28	30	31	32	33	34	35	36	38	39	41	42	43
Area km^2	Yes	13.1	165.3	12.6	24.9	0.5	58.8	1.1	6.5	31.8	26.9	24.1	22.4	7.6	1.7	7.9	7.4	30.5	4.9	3.2	21.2
Elevation min m	Yes	262	284	375	378	487	418	579	432	285	297	263	366	326	390	286	305	428	389	247	285
Elevation max m	Yes	675	887	701	712	570	887	742	685	519	589	472	787	676	546	694	477	790	675	482	561
Elevation range m	Yes	413	603	326	334	83	469	163	253	234	292	209	421	350	156	408	172	362	286	235	276
Elevation mean m	No	503	563	543	537	512	607	660	557	413	447	375	593	504	466	476	419	599	541	392	417
Elevation std. dev.	No	92	94	76	81	19	77	37	57	50	57	50	87	75	37	98	30	65	75	52	50
Slope min deg	No	0.2	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.4	0.2	0.0
Slope max deg	No	21.4	38.2	21.8	21.1	10.5	23.8	9.1	21.8	16.7	21.6	12.8	29.2	19.3	9.7	17.4	18.1	19.3	17.6	21.3	21.7
Slope range deg	No	21.2	38.2	21.8	21.1	10.5	23.8	8.9	21.8	16.7	21.6	12.8	29.2	19.3	9.5	17.4	18.1	19.3	17.2	21.1	21.7
Slope mean deg	No	6.6	5.5	6.7	6.3	3.4	4.8	4.8	6.9	3.1	3.3	2.4	6.3	6.1	3.9	6.0	3.7	5.0	7.6	5.9	3.6
Slope std deg	No	2.9	3.5	3.0	3.2	2.1	2.8	1.7	3.2	2.4	2.5	1.8	4.3	2.8	1.7	2.4	3.0	2.4	2.9	3.0	2.8
Mean aspect	Yes	131.2	85.0	114.7	105.5	121.8	83.2	125.0	110.5	88.5	67.4	84.7	127.3	129.3	44.9	140.8	69.2	83.6	127.4	102.8	78.2
A3deg km^2	Yes	1.3	36.5	1.2	4.2	0.2	16.8	0.2	0.6	19.1	15.4	17.7	5.2	1.0	0.5	0.8	3.9	5.7	0.3	0.4	10.7
%A3deg	Yes	10.3	22.1	9.2	16.7	47.1	28.6	16.7	9.6	60.1	57.3	73.0	23.1	12.4	30.7	9.4	52.8	18.5	7.0	13.8	50.4
A5deg km^2	Yes	3.9	83.4	3.7	9.3	0.4	33.6	0.6	1.7	26.0	21.7	22.1	10.8	3.0	1.3	2.6	5.8	17.5	0.9	1.3	16.5
%A5deg	Yes	29.5	50.5	29.5	37.1	80.7	57.1	52.8	26.4	81.8	80.9	91.3	48.0	38.4	75.8	33.2	77.4	57.3	18.6	42.4	77.6
Basin length km	Yes	5	21	4	8	1	14	2	2	9	12	11	7	6	2	5	6	4	3	2	10
Elongation	Yes	1.5	1.2	1.6	1.3	1.2	1.1	1.1	2.1	1.2	0.8	0.9	1.4	1.0	1.1	1.1	1.0	2.7	1.6	1.6	1.0
Perimeter km	Yes	16	67	15	23	4	41	5	10	28	34	27	23	14	6	13	16	23	9	8	27
Crenulation	Yes	19.9	27.4	17.0	20.4	34.1	29.2	23.3	17.0	24.2	43.0	30.5	22.6	25.6	24.2	22.1	34.9	17.4	16.2	21.9	34.8
Geometry number	Yes	6	70	6	11	0	25	0	3	15	11	10	10	4	1	3	4	13	3	2	9
Relief ratio	Yes	0.09	0.03	0.08	0.04	0.07	0.03	0.08	0.10	0.03	0.02	0.02	0.06	0.06	0.07	0.08	0.03	0.09	0.11	0.10	0.03
Relative relief	Yes	0.81	2.46	0.86	1.11	0.12	1.42	0.22	0.62	1.15	0.79	0.89	1.00	0.54	0.26	0.60	0.46	1.33	0.55	0.38	0.78
CLA3deg km	Yes	5	132	4	14	2	63	1	2	49	39	47	15	3	2	3	7	19	1	1	31
%TCLA3deg	Yes	17.3	33.8	15.3	25.5	91.6	45.3	24.3	13.1	71.7	61.7	79.9	29.6	18.6	34.0	14.7	50.8	26.0	13.1	10.9	60.1
CLA5deg km	Yes	11	249	10	28	2	102	2	4	61	55	56	31	7	4	10	10	50	2	3	42
%TCLA5deg	Yes	40.0	63.8	34.7	49.6	100.0	73.7	61.3	30.8	89.2	86.6	94.2	60.3	46.7	79.8	56.9	69.9	68.2	22.7	42.3	82.4

Table 4.7 Derived statistics (a) for catchments 21-43. *=included by Mitchell & McDonald(1995)

Variable name	*Source(*)*	*21*	*22*	*23*	*24*	*25*	*26*	*27*	*28*	*30*	*31*	*32*	*33*	*34*	*35*	*36*	*38*	*39*	*41*	*42*	*43*
1st orders	**Yes**	30	475	41	73	2	169	4	23	83	70	63	62	21	5	16	15	80	13	8	51
2nd orders	**Yes**	6	106	8	15	1	38	2	5	17	15	14	11	4	1	5	2	17	2	3	14
3rd orders	**Yes**	2	25	3	3	0	9	1	2	2	5	1	3	1	0	1	1	5	1	1	2
Strahler Order	**No**	4	6	4	4	1	5	2	4	4	4	3	4	3	2	3	3	4	3	3	4
Shreve Magnitude	**No**	30	475	41	73	1	169	3	23	83	69	63	62	21	5	16	15	80	13	8	51
Max Stream length, km	**Yes**	6.83	28.72	6.46	9.66	1.22	17.69	2.04	3.69	12.72	14.87	13.12	9.66	6.78	2.91	6.28	6.98	11.79	3.54	3.60	11.50
Main stream gradient %	**Yes**	6.05	2.10	5.05	3.46	6.79	2.65	7.99	6.87	1.84	1.96	1.59	4.36	5.16	5.35	6.50	2.46	3.07	8.09	6.53	2.40
Total channel length km	**Yes**	27	390	27	57	2	139	3	13	69	63	59	52	15	5	18	14	73	8	6	51
Stream density km / km^2	**Yes**	2.1	2.4	2.2	2.3	4.0	2.4	2.6	2.1	2.2	2.4	2.5	2.3	2.0	3.0	2.3	1.9	2.4	1.5	1.9	2.4
Stream frequency	**Yes**	4.52	5.74	6.43	5.82	6.47	5.73	6.24	6.95	5.18	5.18	5.18	5.48	5.40	5.43	3.92	3.90	5.22	5.14	4.75	4.76
Drainage intensity	**Yes**	2.17	2.43	2.95	2.57	1.61	2.43	2.38	3.38	2.39	2.20	2.11	2.36	2.75	1.81	1.69	2.08	2.17	3.33	2.53	1.99
Bifurcation ratio	**Yes**	5.00	4.48	5.13	4.87	2.00	4.45	2.00	4.60	4.88	4.67	4.50	5.64	5.25	5.00	3.20	7.50	4.71	6.50	2.67	3.64
Length overland flow	**No**	0.24	0.21	0.23	0.22	0.12	0.21	0.19	0.24	0.23	0.21	0.20	0.22	0.25	0.17	0.22	0.27	0.21	0.32	0.27	0.21
Burnt fraction	**No**	0.00	0.07	0.01	0.02	0.07	0.01	0.00	0.03	0.14	0.12	0.13	0.17	0.69	0.88	0.00	0.23	0.04	0.00	0.00	0.37
Burnt area km^2	**No**	0.0	12.3	0.2	0.4	0.0	0.8	0.0	0.2	4.5	3.1	3.1	3.9	5.3	1.5	0.0	1.7	1.3	0.0	0.0	7.7
Gripped fraction	**No**	0.16	0.08	0.09	0.05	0.04	0.09	0.22	0.13	0.11	0.22	0.10	0.15	0.11	0.80	0.21	0.25	0.05	0.13	0.00	0.32
Gripped area km^2	**No**	2.1	13.9	1.2	1.3	0.0	5.4	0.2	0.8	3.4	5.9	2.3	3.4	0.8	1.3	1.7	1.9	1.7	0.6	0.0	6.7
Fraction peat cover	**No**	0.83	0.87	0.86	0.85	0.84	0.89	0.91	0.94	0.82	0.83	0.77	0.92	0.97	0.95	0.56	0.95	0.93	0.81	0.83	0.85
Peat area, km^2	**No**	10.8	143.1	10.9	21.1	0.4	52.4	1.0	6.1	26.2	22.3	18.7	20.6	7.4	1.6	4.4	7.1	28.4	3.9	2.6	18.0
Fraction peat ungripped	**No**	0.81	0.90	0.89	0.94	0.95	0.90	0.76	0.86	0.87	0.74	0.88	0.83	0.89	0.16	0.62	0.74	0.94	0.84	1.00	0.63
Sheep/sqKm 88 mean	**No**	409	238	229	229	229	287	283	229	379	381	329	168	135	135	239	344	218	469	313	409
Sheep/sqKm 80 mean	**No**	294	193	217	217	217	231	255	217	337	339	292	156	140	140	222	273	152	320	249	63
LTM_{WOUK3}	**No**	86.5	76.6	82.9	83.5	79.3	76.0	78.4	81.5	75.3	72.0	72.8	73.7	66.0	59.6	84.5	74.2	78.4	85.2	64.5	66.7
LTM_{band3}	**No**	33.7	30.1	35.0	34.2	32.1	32.2	33.4	35.9	31.0	30.9	30.5	31.1	28.7	29.3	32.6	32.3	33.2	34.3	27.6	29.7
LTM_{band4}	**No**	181.0	137.1	196.3	191.5	168.6	161.9	184.4	210.3	151.5	149.7	143.7	146.3	118.5	133.0	161.7	169.1	178.1	194.5	100.2	133.4
$LTM_{band3eq}$	**No**	79.2	61.1	72.2	71.0	61.9	55.8	55.9	67.5	65.3	57.7	67.3	55.0	53.9	51.3	86.3	64.4	57.4	72.2	54.0	59.3
$LTM_{band4eq}$	**No**	53.6	70.0	64.3	116.8	110.3	80.8	111.9	81.3	142.1	138.4	75.6	99.8	125.7	186.7	168.1	143.4	164.3	190.7	158.5	118.4
$LTM_{lcband7}$	**No**	150.0	125.9	155.5	149.5	140.5	131.4	148.3	153.5	117.1	114.1	106.8	140.1	125.3	112.1	134.4	118.3	139.9	154.0	116.4	110.0
$LTM_{lcband4}$	**No**	143.2	104.8	131.7	130.6	110.9	100.4	108.1	123.1	118.1	102.3	128.1	97.2	89.7	82.3	154.0	118.4	100.5	134.7	99.6	103.2
$LTM_{lcband2}$	**No**	112.1	72.7	104.8	101.0	82.3	75.8	83.2	96.3	73.3	63.0	72.1	68.4	53.7	48.8	102.3	75.6	74.7	101.1	53.2	64.3

Table 4.8 Derived statistics (b) for catchments 21-43. *=included by Mitchell & McDonald(1995)

4.5 Statistical methods for development of a predictive model

4.5.1 Rationale

The sub-catchment statistics and measured DOC concentrations for each sampling run were compared. The overall aim was to develop a model to predict DOC export based on the sub-catchment spatial statistics, and to relate this to the colour observed at the catchment outlet at Broken Scar, in order to identify those areas within the catchment causing concentration of the colour observed at Broken Scar and those areas causing dilution of the observed colour.

Since the aim was to identify sources that were concentrating or diluting relative to Broken Scar in terms of DOC concentration, absolute measured DOC concentrations were not used. Each survey sampled a different set of sites, and conversely each site was sampled in a different combination of the seven survey runs. Since weather, seasonal, and flow conditions varied between runs, simply using the mean DOC concentration observed for each site over all the runs in which it was sampled would not be appropriate. If a site was only sampled on days with lower overall colour conditions (for instance, following prolonged wet periods) then the mean colour from that site would be lower, all other things being equal, than the mean colour from a site sampled on days with higher overall colour conditions.

Instead, for each sampling run, all measured DOC concentrations were ratioed to the measured DOC concentration from Broken Scar for that sampling run. Samples with a higher DOC concentration than Broken Scar were therefore allocated a value > 1 and samples with a lower concentration than Broken Scar were allocated a value < 1.These normalised DOC values were then used in the modelling work. If the response variable were the raw DOC concentration at each site it may be expected that the model developed for each sampling run would be different, as for each site the predictor variables remain constant between runs whilst the response variable does not. As the modelled response was in fact DOC concentration normalised to that at Broken Scar, it was hoped that this would reduce the effect of variation between sample runs, as the model would only vary between sampling runs if the response of a given subcatchment relative to that of Broken Scar varies – i.e. if the subcatchments respond differently to varying flow regimes.

The aim of the study was to develop a predictive model of colour export that could be validated with further sampling runs. A preliminary version of this modelling work was conducted after the first three sampling runs. Further sampling sites which were sampled only after the first three runs (Table 4.2) were identified to maximise the differences in predicted colour based on the models thus identified, and the remaining runs were conducted as model validation runs. Finally a refined model was produced when all the data had been collected (See section 4.6).

4.5.2 Techniques for selection of variables for multiple linear regressions

A large number of catchment characteristic variables have been developed, as described in Table 4.5 - Table 4.8. These have been produced without any direct evidence of their relevance or otherwise to DOC export, but it is hoped to use some or all of these variables to predict DOC concentrations.

Using all of the variables listed in Table 4.5 - Table 4.8 would not yield robust models, as significant collinearity exists between some of the variables. This is due partially to the nesting of the catchments – for instance the maximum elevation of the Broken Scar catchment is the same as the maximum elevation of all the subcatchments containing the same headwater point. However other variables are correlated in their own right. For example, only peat soils are gripped, so the area gripped within each catchment may be expected to be correlated with the area of peat. Similarly peat soils form in flatter areas and so percentage peat cover is likely to be correlated with mean slope. More basically, catchments with a lower average slope would also have a lower main stream gradient. Furthermore, there are a large number of variables. Techniques such as multiple linear regression require many more observations (samples) than variables – Tabachnick and Fiddell (1989) suggest an absolute minimum of 5 times more observations than predictors, ideally with the number of observations being at least 100. Other commonly-applied rules of thumb as summarised by Green (1991) recommend even more observations.

Therefore attempting to model DOC concentrations from the variable set given in Table 4.5 - Table 4.8 would be unlikely to be successful, as two key assumptions of multiple linear regression are not met: there are significant collinearities between many of the variables, and there are insufficient observations relative to the number of variables. Without reducing or simplifying the dataset in some manner, models will be overfit – that is, they correspond with great accuracy to the calibration dataset but have little or no predictive ability when applied to another dataset collected under similar conditions.

Two main types of technique for avoiding this problem were assessed: variable selection algorithms, and reduction of the data to uncorrelated components. Stepwise (forward and backward) linear regression and best-subsets regression are variable selection techniques, which seek to reduce the variable set by identifying those variables which result in the most significant model. Principal components regression and partial least squares regression are decomposition techniques, based on representing the variation in the data as new, uncorrelated components which can then be used as regression predictor variables.

4.5.2.1 Stepwise Linear Regression

For any set of n possible predictor variables, there are 2^n-1 possible subsets of variables. Stepwise linear regression seeks to find the subset of variables that provides the "best" model (based on a given goodness-of-fit statistic calculated for each model) whilst excluding those variables that do not contribute significantly to the quality of the model. This is a search problem, and stepwise regression approaches this using a heuristic algorithm. This means that at each stage of the procedure the search moves forward, in this case by adding or removing a variable, according to the results of a particular test. In stepwise regression the search space is the set of all $2^n - 1$ possible variable combinations, and the heuristic rule is the significance of the coefficient of each variable, based on the t-test, within the model. At each stage the F statistic is computed for each variable, and the variable with the largest statistic is selected.

The procedure can run in two directions: either starting with an empty model and adding variables (forwards stepwise regression), or by starting with a full model (a model based on all the predictors) and at each stage removing variables (backwards stepwise regression). In either case, the procedure can be reversed such that once added, a variable may at a later stage be removed again, or vice versa.

In the case of forwards stepwise regression, a simple regression is first performed between each possible predictor separately and the dependent variable. The t-statistic is calculated for the coefficient of the variable in each case, and squared to obtain the F-statistic. When this is complete, the predictor variable x with the highest F-statistic is selected for entry into the model, provided that the F-statistic is greater than a pre-selected threshold value. The procedure is then repeated by calculating the simple regression between each model containing x in addition to one of the remaining predictor variables, and the t- and F-statistic for each of the remaining predictors in these potential models is calculated. Once again the predictor with the highest F-statistic greater than the pre-selected threshold is selected for entry into the model, whilst if the F-statistic of any variable already in the model from a previous step has dropped below the pre-selected threshold, that variable is removed from the model. The procedure then continues until no variable outside the model has an F-statistic greater than the threshold to enter, and no variable within the model has an F-statistic greater than the threshold to remove.

The stepwise algorithm is therefore a local search procedure – at each stage of the search the best move from that position is identified and taken. The limitation of this single path through the search space is that not all possible models are assessed: potentially better models are missed if these involve at any stage a step towards a "worse" model. Equally the procedure does not cope well with collinearity and may select variables that an inspection of the data will reveal do not make sense to be included together (for instance area, fraction of peat cover, and total peat area). Therefore the results of the model should be carefully inspected and the procedure may need to be repeated with some variables manually removed from the search space. The stepwise procedure works well to identify the most useful subset of uncorrelated variables, but tends to be unstable if there are significant correlations between some of the variables.

4.5.2.2 Best Subsets Regression

Best Subsets Regression is a conceptually simpler procedure to identify models but one that is considerably more expensive in terms of computing time. For n possible predictor variables, the algorithm simply conducts an exhaustive analysis of the search space, testing and recording goodness-of-fit statistics for models produced from all of the 2^n-1 possible subsets of variables, and reporting results for a small number (usually two or three) of the "best" models of each size, as defined by a goodness-of-fit test such as highest adjusted-R^2 value. As the number of possible predictors grows, this technique rapidly becomes unwieldy, but with the number of potential predictors used in this study, the technique is feasible, requiring only a few seconds in efficiently-programmed statistics software.

A best-subsets search will always find the best possible model for each size, in terms of the goodness-of-fit test used, because the search is exhaustive rather than following a single path so all models will be created and the search does not terminate in some inappropriate branch. However it is just as likely as the stepwise algorithm to create models with inappropriate or unrealistic combinations of variables. The results can be analysed to ensure that conceptually unrealistic or highly-correlated combinations of variables are not included, without the requirement to think about this selection before the search is conducted – all that is lost is computational time.

4.5.2.3 Decomposition techniques

An alternative approach to avoid the problems caused by collinearity is the use of decomposition techniques, which seek to find a new, smaller and uncorrelated set of variables which describe as much as possible of the variation in the original variable set whilst remaining uncorrelated. One such technique is Principal Components Regression. This method consists of producing a set of uncorrelated components from the predictor variables that whilst uncorrelated still explain the variance between the predictors. The components are calculated in exactly the same way as for a standard principal component analysis. The component scores are then calculated for each observation in the dataset. Once the number of principal components to retain is selected, the scorings for these components are then used as the predictor variables to develop a regression model on the original dependent variable.

Since the components are not correlated with one another, the collinearity problem is eliminated. Since each component represents a number of correlated variables, and since correlated variables are likely to be related to one another in some physical manner, it is the aim that each component should explain different "aspects" of the data which are then not represented in the other components. Also, since each component represents a number of the original variables, the principal components analysis is a variable reduction technique whereby a smaller set of variables (the components) is created which explain a larger proportion of the variance in the data than can be explained by any combination of the same number of original variables. Furthermore, the number of components retained can be selected to retain those components representing real variation structure in the data, and discard those components representing "noise".

The disadvantage of the principal components regression method is that the principal components were themselves generated only to explain the variance in the original predictor variables; the algorithm is blind as to variation in the response variable. There is therefore no guarantee that the scores thus generated have any direct relevance for the dependent variable or that they will produce a good regression model for the response.

A second decomposition technique is Partial Least Squares regression (or Projection to Latent Structure), PLS (Martens and Naes (1989); Wold et al, (1983)). This is another approach recommended for use when the predictor data is ill-conditioned – for instance when there exists collinearity between variables or when the number of predictors is high compared to the number of observations, for the same reasons as PCR. Similarly to PCR, PLS is based on representing the data as uncorrelated components, and then using the scorings from these components as predictor variables for the original response variable. However in the case of PLS regression the components are constructed from the predictor and response variables, such that the components represent the maximum possible amount of the covariance between the predictors and response(s). This addresses the disadvantage of principal component regression described above, as components are selected to represent high variation in the responses as well as in the predictors.

This means that the PLS approach is not in itself a method of screening out irrelevant variables (although the standardised regression coefficients for such variables in the resulting model will be low, so their influence on the model is itself low), but rather that the quality of the model is not necessarily affected by the presence of such variables. Variables that are not relevant to the response will not be associated with much variation in the response space, and so will not have high loadings in the components selected, effectively being "ignored" by the model; PLS is therefore an excellent technique for developing predictive models from a large number of predictive variables, but not for developing explanatory models of the causatory relationships between the variables.

The number of components that it is appropriate to retain for the regression model must be selected – if all components are retained then the method is equivalent to multiple linear regression. However as with PCA / PCR the majority of variance is usually explained by a much smaller subset of the components, meaning that fewer new variables can be used to represent the information that was contained in the original variables. PLS extends this principle to ensure that only information from the predictors that is of use in predicting the response will be represented in the components. In PLS the number of components to retain is assessed using a cross-validation procedure whereby each possible model is tested for its ability to predict the original data. For each potential number of components, the predictive ability of the resulting model is assessed by leaving out each data point one (or more) at a time, recalculating the model, and recording how well the model then predicts the missing data. This provides a mechanism to ensure that the model is not overfit and predicts only genuine structural variation in the data.

4.6 Outline of model development

The intention of this study was to develop and test a predictive model for DOC export by following an iterative process of sampling, model development, and further sampling. Preliminary models were developed by grouping data from the early sampling runs and deriving the best-fit multiple linear regression and binary logistic regression models from these data to predict observed DOC concentrations and contributing areas. These models were then used to identify further catchments to be included in subsequent sampling runs that would provide a good test of the model. For example, if the preliminary model identified gripped fraction as an important variable, then further catchments would be identified to maximise the variation in gripped fraction for subsequent validation runs. The iterative nature of the sampling process meant that the first three sampling runs were used as calibration runs, and the preliminary model was then developed based on these data. New catchments were introduced in the remaining sampling runs and a wider range of catchment descriptors was made available. The intention was to validate the preliminary model using an iterative strategy, improving the preliminary model where possible using the data from the first three runs as a calibration set with new spatial data, and then using the new data as a validation set. However, due to differences between the weather conditions and characteristics of runoff production between the various sampling runs, this chronological iterative design was not adhered to as it was found that the data could not meaningfully be grouped in this way. Instead, the entire dataset was divided into calibration and validation sets based firstly on similarity between the flow conditions at the times of sampling and secondly on the observed relationships between the measured responses for each run and the predictor variables.

In this way a predictive model was produced and then developed both for normalised DOC concentration (based on multiple least squares regression) and for predicted contribution to overall DOC levels (based on binary logistic regression). In many ways the data modelled only marginally met the data requirements for these regression techniques, due in particular to collinearities between the predictor variables and to a low number of observed data points compared with the number of predictors. To address these concerns, modelling was repeated using the entirely different technique of partial least squares regression. To summarise, the overall modelling pattern using ordinary least squares (OLS) methods (including variable selection techniques), logistic regression, and partial least squares (PLS) regression is shown in Figure 4.10.

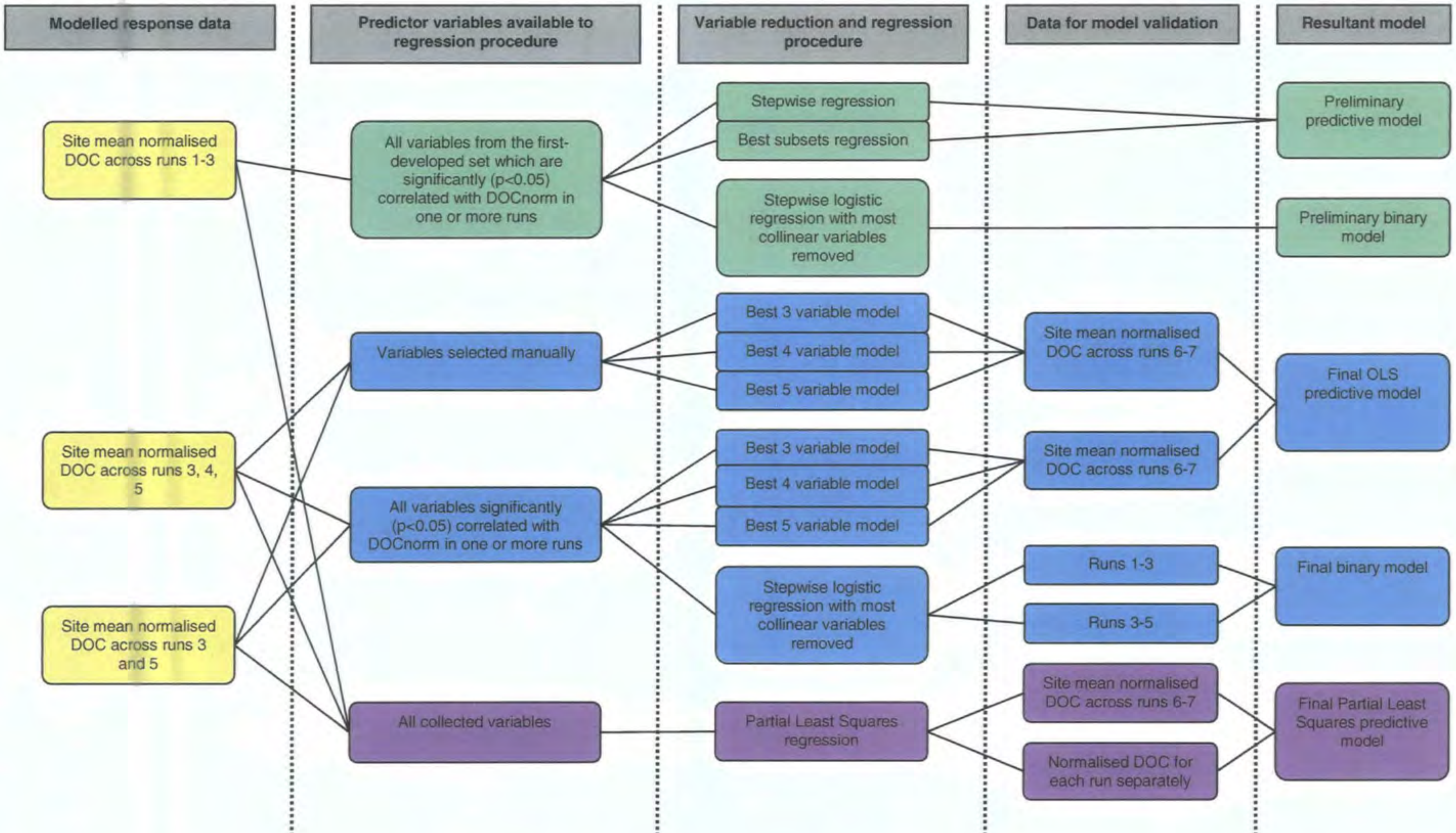


Figure 4.10 Overall framework of the regression modelling.
Green= Preliminary model development after 3 runs. Blue = multiple linear and binary logistic regression after collection of entire dataset. Purple = PLS modelling.

4.7 Preliminary model results

Preliminary models were developed after the first three sampling runs. A complication to the iterative strategy was that at this stage not all of the catchment characteristics shown in Table 4.5 – Table 4.8 had been produced. Those that were available at this stage were Area, $Elevation_{min}$ – $Elevation_{mean}$, $Slope_{min}$ – $Slope_{std}$, peat cover area/fraction, gripped area/fraction, and fraction of peat remaining ungripped (FP_{ungrip}).

Each of these variables was correlated against the measured DOC concentration for each sample run and the variables significantly correlated with the response ($p < 0.05$) were identified. A regression was fitted between these variables and the measured DOC concentration (Table 4.9).

Sampling run	*Significant variables*	*R^2 of regression fit for this run only*
1: 04/06/2003	$Slope_{mean}$, $Elev_{max}$, FP_{ungrip}	0.55
2: 30/06/2003	Area, $Gripped_{area}$, $Peat_{area}$ $Slope_{mean}$, $Elev_{max}$, Relief, $Elev_{std}$, $FracPeat_{ungrip}$	0.72
3: 19/11/2003	$Gripped_{frac}$, $Peat_{frac}$, $Elev_{mean}$	0.46

Table 4.9 Significant variables in the preliminary modelling

4.7.1 Observed data

In order to produce the overall preliminary model the results from the three runs were combined by taking the mean DOC concentration, normalised to Broken Scar in each case, for each catchment across the three runs. Not all of the catchments had been sampled in all three runs (eg catchments 7, 8, 12, 20, Table 4.2) and so it should be noted that the mean value was not necessarily derived from the same number of sampling points for each site. The normalised values rather than the actual DOC concentrations were therefore modelled in order to reduce the effect of any systematic variation in concentrations between sampling runs. These observed relative DOC concentrations as entered into the model for the 28 catchments involved in the first three runs are shown in

Figure 4.11. This figure and all those that follow show the outlines of the catchments as they were given in Figure 4.2.

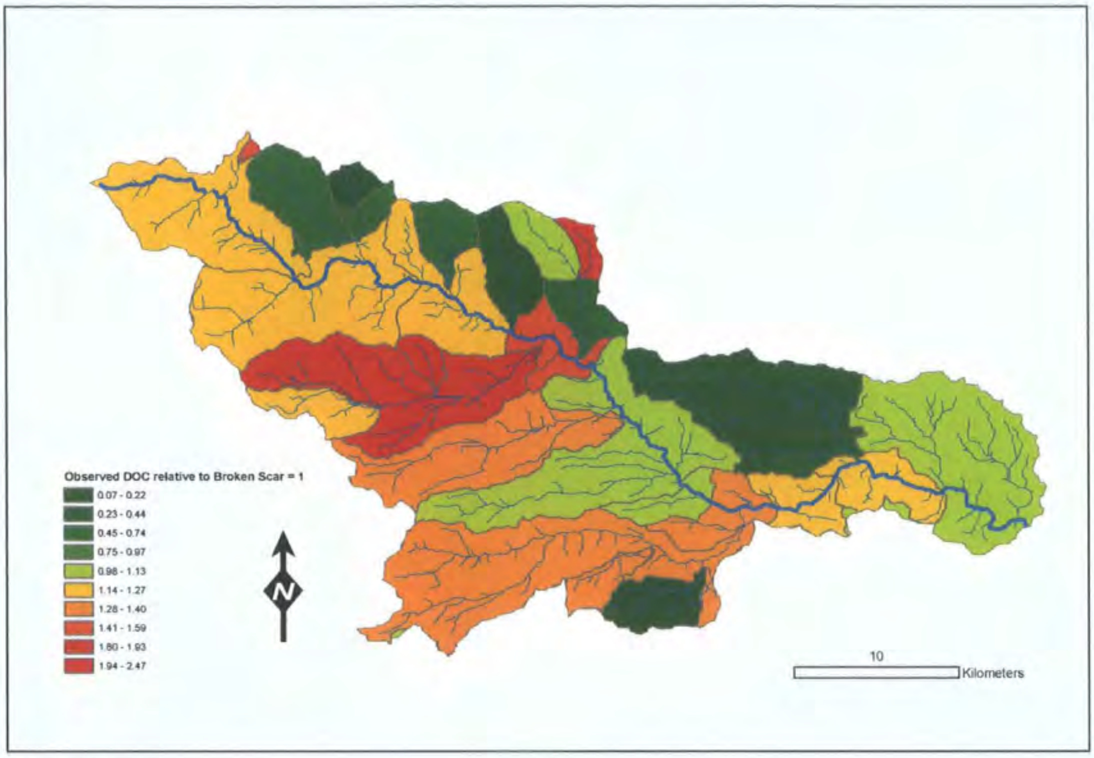


Figure 4.11 Observed normalised DOC concentrations from the calibration runs

There is a general spatial trend distinguishing catchments to the north and south of the main river, with the catchments to the north showing lower concentrations than those to the south. Furthermore there could be a general trend of increasing concentrations upstream along the main river branch. From the maps of peat area (Figure 4.3) there is no clear distinction in overall peat cover between the northern and southern catchments, although there possibly is a difference in terms of the actual LCM classes, with the northern catchments having higher proportions of LCM class 9 (Moorland grass) and those to the south having higher proportions of LCM classes 10 and 11 (open and dense shrub moors). Northern catchments are also generally steeper. There are catchments which do not conform to the northern/southern trend of DOC concentration (Little Eggles Hope in the north, and Gill Beck in the south, and so in the validation stage of the modelling process further subcatchments will be selected in an attempt to confirm or deny whether there is a true inherent spatial trend or whether it is due to similarities between the characteristics of the subcatchments themselves, rather than their location within the catchment.

4.7.2 Multiple linear regression (MLR) model

The best fit regression between the mean normalised DOC concentrations and the significantly-correlated catchment characteristics was identified by running a stepwise (forward and backward) regression procedure with all the independent variables identified in Table 4.9 as input. A best subsets regression procedure was also run on the same variables to check the quality of the model produced by the stepwise procedure. Both of these methods resulted in the same model, which is shown in Equation 4.1:

$$DOC_{norm} = 0.34 - 0.22Slope_{mean} + 0.0009Relief + 1.98Peat_{frac}$$
$$\mathrm{R}^2 = 0.40 \quad \mathrm{R}^2_{adj} = 0.33$$

Equation 4.1 Preliminary model, developed after 3 runs by variable selection / multiple linear regression

This model was used to generate "predicted" DOC concentrations for all the catchments involved in these first three survey runs (Figure 4.12). The map follows the trend in the observed dataset of a pattern distinguishing between the northern and southern sides of the catchment with northern catchments (having a generally southerly aspect) having lower predicted and observed concentrations. Meanwhile the predicted concentration in the main river branch generally increases towards the headwaters.

The model was also applied by generating the relevant statistics for individual 1km^2 cells of the catchment in order to provide a visual representation of key predicted source areas (Figure 4.13). This further emphasises the north/south pattern, suggesting DOC contribution to be particularly concentrated in the headwater areas of the Lune, Balder, and Greta, while the areas to the north of the main river are lower in predicted concentration.

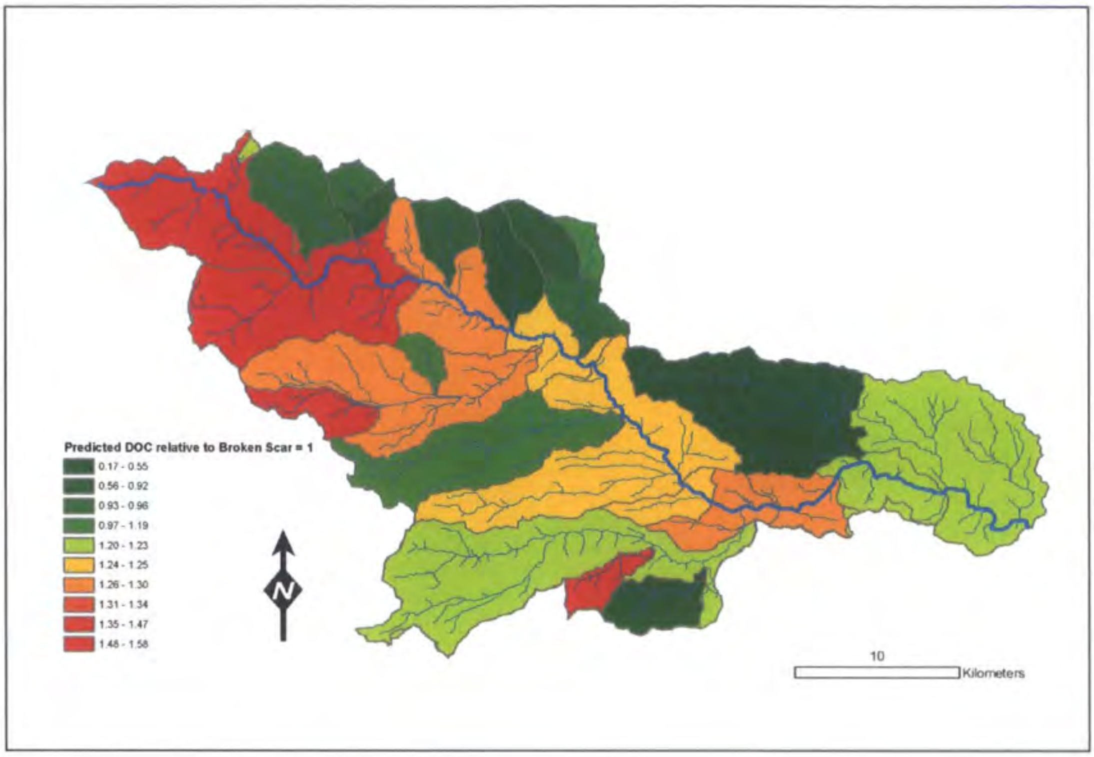


Figure 4.12 DOC concentrations predicted by preliminary model for sites sampled in first three surveys

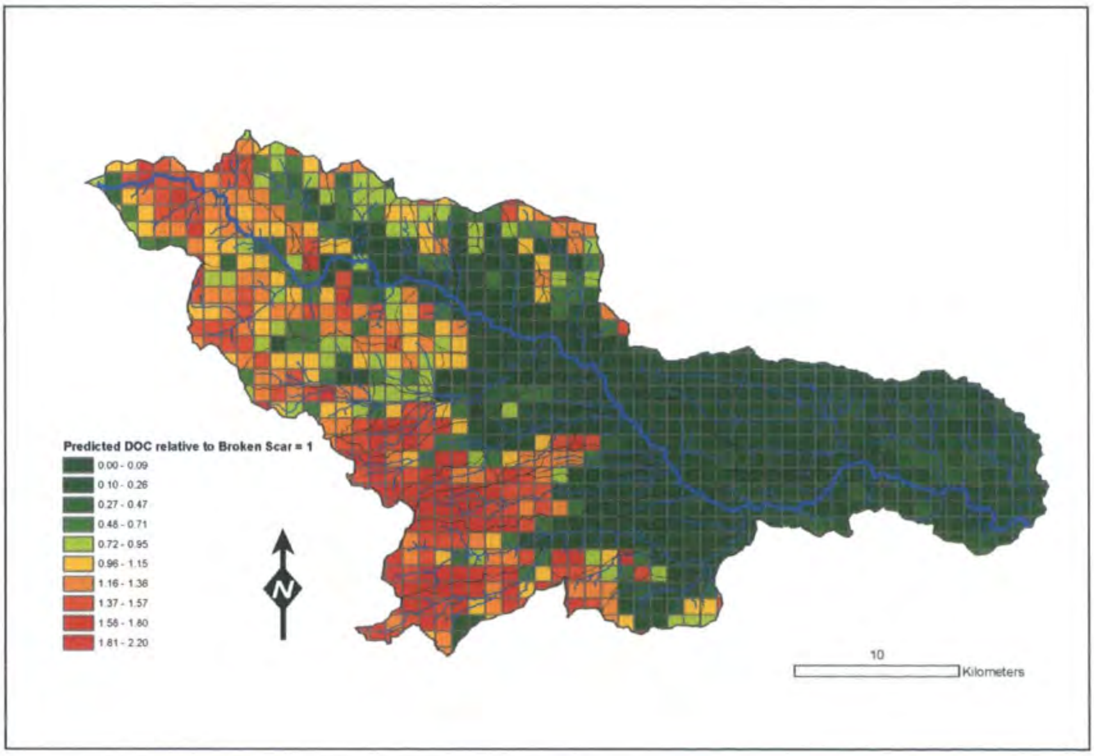


Figure 4.13 Preliminary model applied to 1km squares

Clearly the overall predictive power of this model is not good with $R^2_{adj} = 0.33$; there is a large amount of variation in the response data which is not explained by the model. However the fit of the model is highly significant ($F_{3,24}=5.40$, $p<0.01$) and all the variables in the model are significant ($p<0.05$), whilst the original correlations of the variables with DOC concentration are strong for individual sampling runs.

Furthermore, the identified variables are easily explained in physical terms. The negative correlation between mean slope and DOC concentration can be interpreted either in terms of steeper catchments having a greater runoff proportion and lower residence times, meaning that water has less time to acquire DOC, or that in more sloping catchments there is likely to be less peat – this represents one of the possible collinearities that will be addressed through variable selection strategies.

The positive relationship with catchment relief is slightly surprising as it acts against the remarks about mean slope above. Two possible explanations for this are suggested. The first is that this may be an artefact of the catchments selected. All else being equal, larger catchments would tend to have a greater relief, and the subcatchments selected in this study are generally larger in those areas which were observed to have higher DOC concentrations (for instance the Lune) and smaller in those areas with low observed concentrations (Bowlees Beck, Hudeshope Beck). Although these latter catchments are steeper their overall relief is less due to their smaller size. Furthermore the main river branch in this study becomes steeper upstream (with therefore a greater relief per unit area) although this is not necessarily reflected in the mean slope of the catchment. The second possible explanation is that the true effect is due to maximum or mean elevation, rather than relief, but that due to the multiple correlation between these variables the "wrong" variable has been selected by the regression procedure. In either case the importance of manually assessing the physical plausibility of a model is highlighted and this will be addressed in the development phase of the modelling. A positive correlation with maximum elevation, and potentially equally with relief could also be interpreted in terms of the greater occurrence of organic rich soils such as peats at greater altitudes within the Tees catchment. This variable must be considered in light of the nested nature of many of the catchments – the maximum elevation of downstream sites on the main river branch will be the same as that of the highest tributary subcatchment and therefore the maximum elevation is related to the nature of a site's headwaters. Lower subcatchments which contain rich DOC source areas upstream can themselves be seen as contributing, reflected in their maximum elevation, whiles lower subcatchments which do not contain such areas will have a lower maximum elevation.

Fraction of peat cover is positively related to DOC concentration, as would be expected given that peat, being an organic rich soil, is taken a priori to be the major source of DOC represented as water colour in the study catchments (Urban et al, 1989). However this model (Equation 4.1) has not included a measure of the extent to which the peat is gripped, although such measures were highly correlated with DOC concentration (Table 4.9).

Generally, this assessment of the nature of the variables suggests that their use to predict DOC concentration is valid despite the poor fit of the model, with the caveat that they cannot explain all observed variation in DOC concentration and their selection is somewhat arbitrary due to collinearities (note the differences between variables found to be significantly correlated with DOC from individual runs, Table 4.9). Also, the lack of fit may be partially attributable to differences between the sampling runs that were analysed in the regression. Although efforts were made to carry out sampling runs on days with similar antecedent weather conditions, this was not always practical due to the relative unpredictability of weather in upland regions, and in any case no account was taken of seasonal differences in planning the sampling runs. If flow conditions were different between sampling runs, then the nature of the runoff from the catchments would also be expected to vary meaning that no one model would necessarily be an accurate predictor of all the data. Following the development and application of this preliminary model, the weather and flow conditions at each sampling run will therefore need to be taken into account in refining the model (Section 4.8.3 and 4.8.3.2) Data from sampling runs will be grouped by weather and flow conditions in an attempt to improve model quality.

The preliminary regression model (Equation 4.1) was applied by identifying a range of potential new subcatchments and generating catchment statistics for these in addition to for individual 1km^2 cells of the overall catchment. The model was then used to generate a predictive map of DOC concentration from these areas (Figure 4.14 – catchments are identified in Figure 4.2 and Table 4.2). The preliminary model was applied to potential new subcatchments in the GIS and catchments were selected to span a large range of predicted concentrations, in order to provide the best possible test of the model whilst being accessible for sampling. However, due to logistical and access problems in the field that were unclear on the maps used, it did not in fact prove possible to sample all of these new sites.

All catchments surveyed in the final runs are shown in Figure 4.15, with the new catchments highlighted. Note that the colour scale in Figure 4.12, Figure 4.14 and Figure 4.15 is the same for ease of comparison whilst the scale in Figure 4.13 is different owing to the wider range of results over the 1km^2 zones.

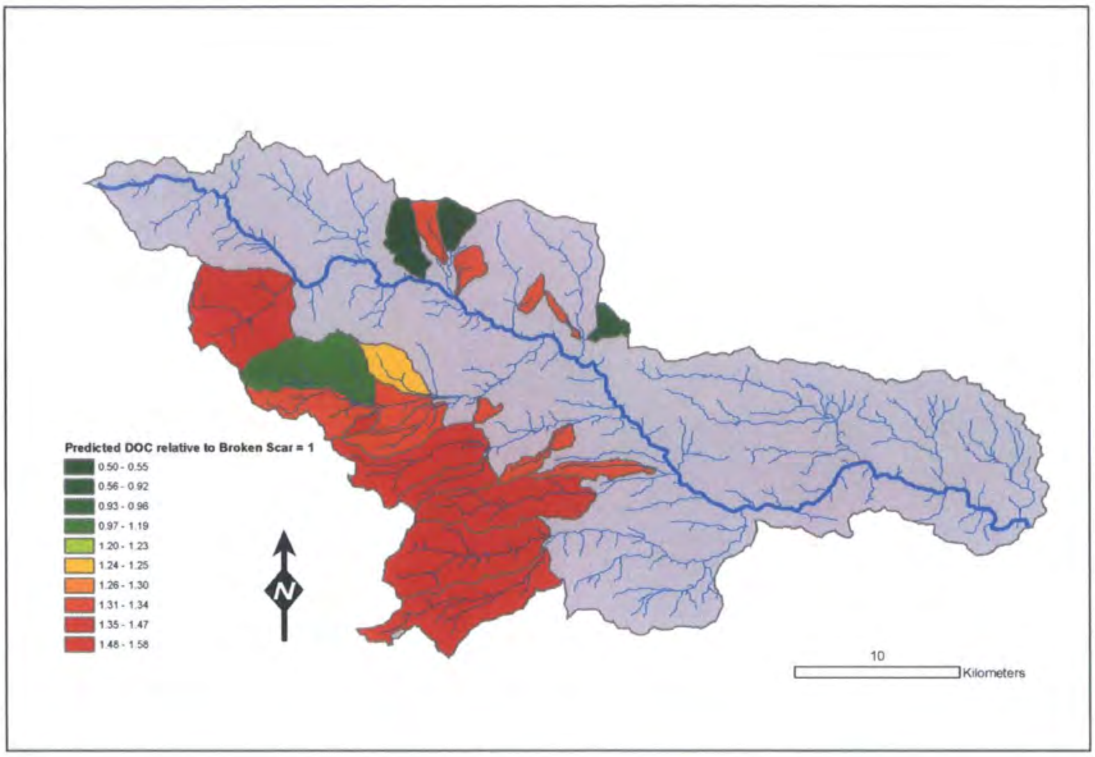


Figure 4.14 Potential new subcatchments

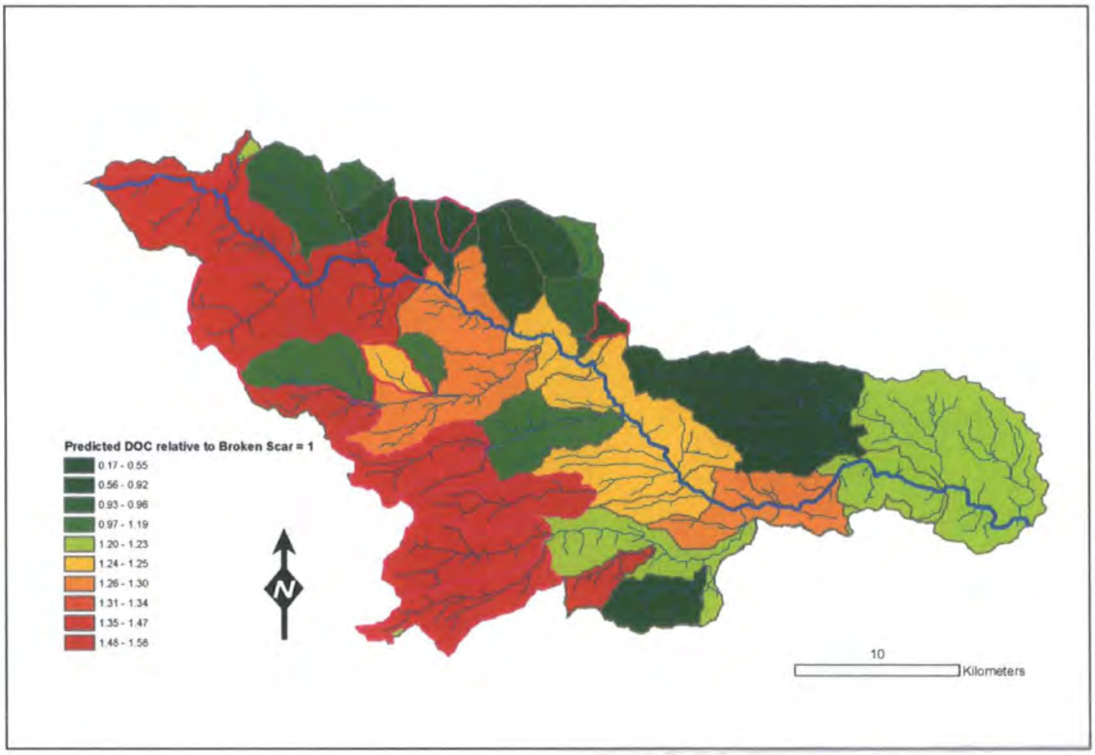


Figure 4.15 All surveyed catchments, with new sites highlighted

4.7.3 Binary logistic regression model

The model described in section 4.7.2 predicts the relative DOC concentration exported from catchments and arbitrary areas. The model does not successfully predict a high proportion of the overall variation in DOC export, possibly reflecting the complexity of the system and the subsequent difficulty in precisely predicting a continuous variable from a small, simplified model. However, the DOC concentration can also be more simply represented, within the requirements of the study to identify colour source areas relative to Broken Scar, as a binary variable. Since the intention is to identify those areas within the catchment responsible for the observed increase in colour load at the WTW, it is appropriate to convert the catchment DOC concentrations to a binary variable based on the concentration relative to Broken Scar. Those sites with an overall DOC concentration higher than that observed at Broken Scar were classified as "Contributing" whilst those with an overall DOC concentration lower than at Broken Scar were classified as "Diluting". The Broken Scar samples themselves were not classified in the model. Whilst it may be difficult to expect to represent all the variation in a linear variable such as DOC concentration to be represented by a simple model, a more robust binary signal may be easier to predict successfully. This enables the application of the binary logistic regression method, which models the likelihood that an observation has a positive or a negative outcome, in order to produce a model to predict areas and subcatchments that have an overall contributory effect to the colour observed at the catchment outlet. The observed classification of sites based on the first three runs, as used for the calibration of this logistic regression, is shown in Figure 4.16.

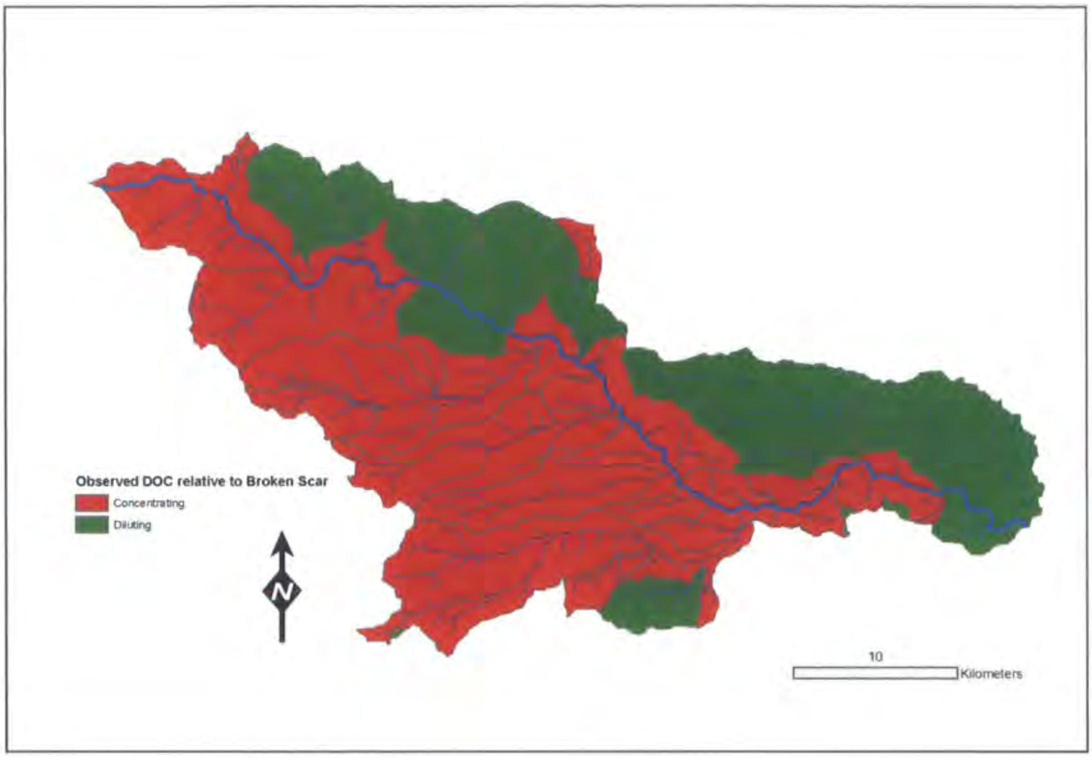


Figure 4.16 Observed concentrating/diluting behaviour of sites in calibration runs

As with the multiple linear regression, the best fit logistic regression between the binary contributing variable and the significantly-correlated catchment characteristics was identified by running a stepwise (forward and backward) selection procedure with all the independent variables identified in Table 4.9 as input. However this resulted in an extremely unstable model due to the small number of observations and the remaining collinearity between the input variables. The variable set was therefore reduced manually to remove the collinearity - gripped area and peat area were removed from the input as these are directly predictable from catchment area and gripped fraction or peat fraction respectively. $Elev_{std}$ was also considered to be a spurious measurement; however this variable was never entered into the model by the stepwise procedure so removing it from the input made no difference.

The best-fit logistic regression equation is given by Equation 4.2:

$$\ln\left(\frac{\theta}{1-\theta}\right) = 34.09 - 1.17 Slope_{mean} - 30.83 FP_{ungrip}$$

Equation 4.2 Preliminary logistic regression model, developed after 3 runs by stepwise selection of variables

where Θ = the probability of the site being a contributing area, in terms of the classification relative to Broken Scar. The model shows 85% concordance with the data, with 9/11 negative outcomes and 14/16 positive outcomes correctly predicted, and the variables are significant at the 95% level.

Since the logistic regression method is probabilistic – that is, it models the probability of a given outcome – in order to classify sites as contributing or not a cut value for the probability must be selected above which a site will be classified as contributing. Setting the cut value to p = 0.5, the left hand side of the logistic regression equation becomes equal to zero and the equation can be rewritten as an inequality:

$$34.09 > 1.17 Slope_{mean} + 30.83 FP_{ungrip}$$

Equation 4.3 Preliminary logistic regression model, expressed as an inequality for identification of DOC-contributing sites

A site is then classified as contributing if the inequality (Equation 4.3) is met.

As with the multiple linear regression model, the variables included in the logistic model can readily be explained in physical terms. Mean slope is included with a higher mean slope reducing the probability of a site being contributing, for the same reasons suggested in section 4.7.2. A higher fraction of peat remaining ungripped also reduces the chance of a site being contributing, or conversely a higher gripped fraction increases the probability of contributing. Since both the source variables for FP_{ungrip} ($Peat_{frac}$ and $Gripped_{frac}$) were also significantly correlated (Table 4.9) this not only backs up the suggestion that peat is the source of DOC, but also suggests that peat drainage accentuates the concentrations.

Similarly to the linear regression predictive model, this inequality can now be applied to old and new subcatchments to identify predicted contributing catchments.

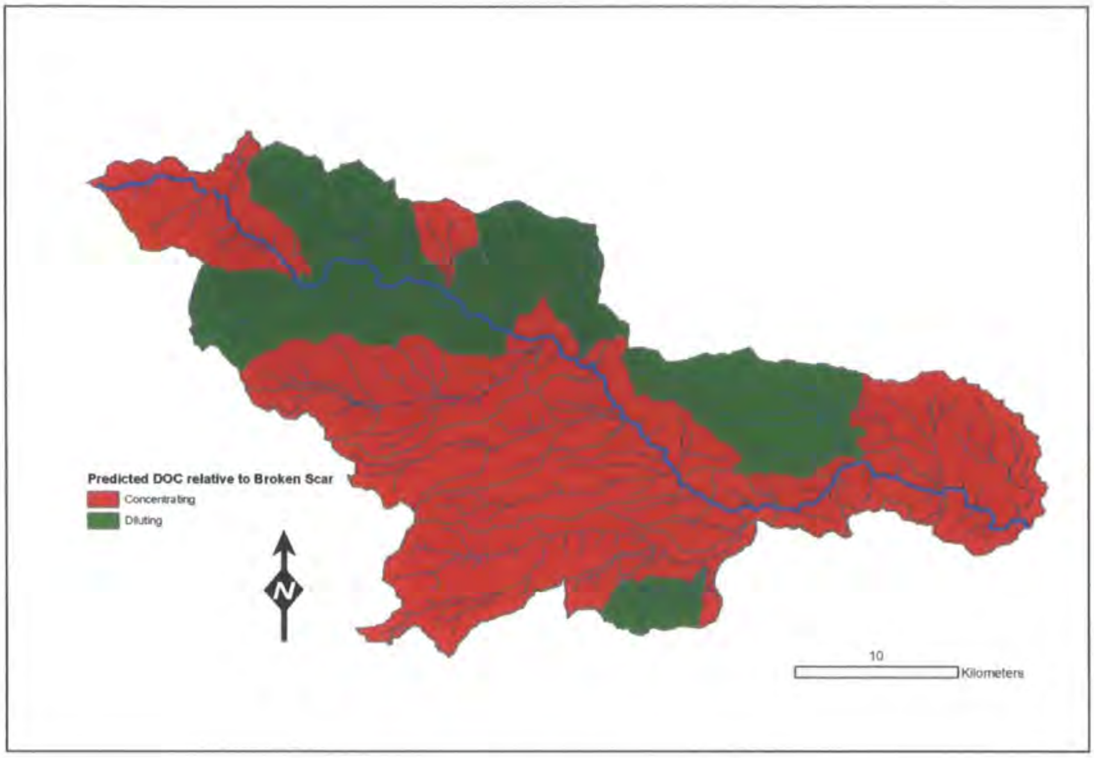


Figure 4.17 DOC relative to Broken Scar, predicted from the preliminary model for sites sampled in the first three surveys

Applied to the sites sampled in the first three surveys (Figure 4.17) the model emphasises the north/south divide between catchment types that was observed in Figure 4.12. This is not entirely surprising when studying the catchment topography, which is generally steeper to the north of the river. Although there is often a correlation between shallow slopes and peat cover, these steeper northern catchments do contain substantial peat cover whilst there are flat areas in the catchments with low peat cover (in particular in the lowland areas) and so the two variables are not necessarily redundant.

Potential new catchments identified as described in section 4.7.2 were also chosen to test this north/south trend with northern sites found that were predicted to be concentrating, and southern sites that were predicted to be diluting (Figure 4.18 and Figure 4.19).

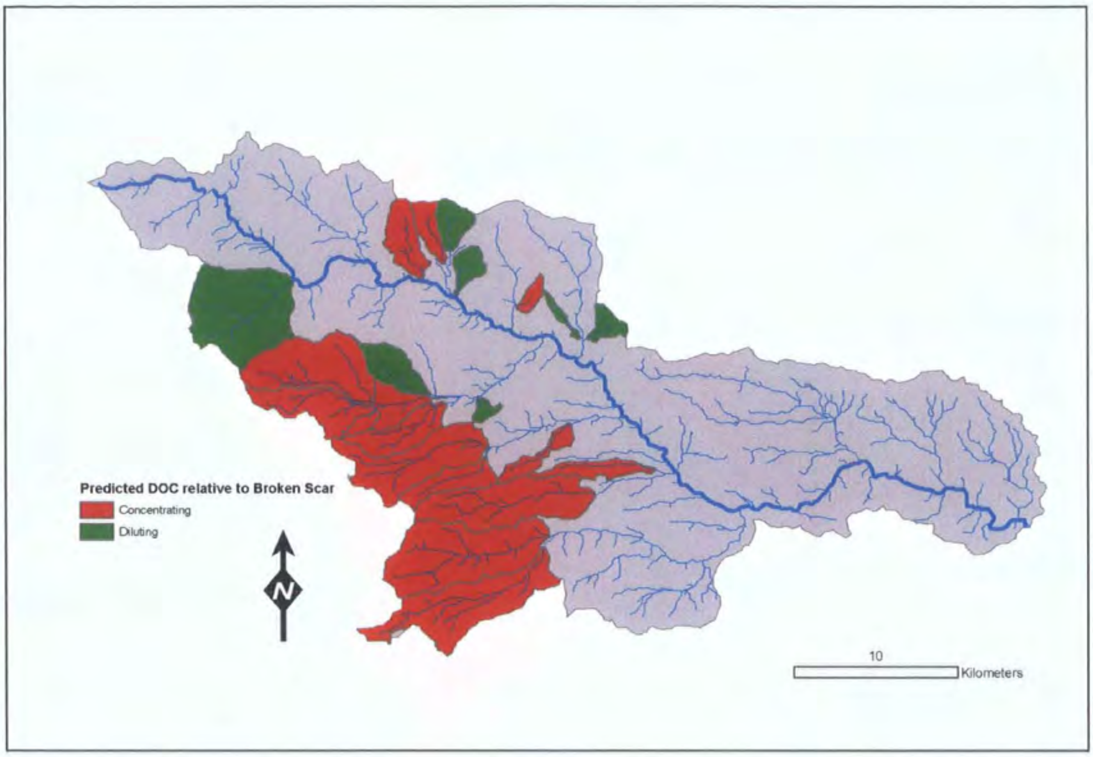


Figure 4.18 Predicted relative DOC contribution of potential new sites

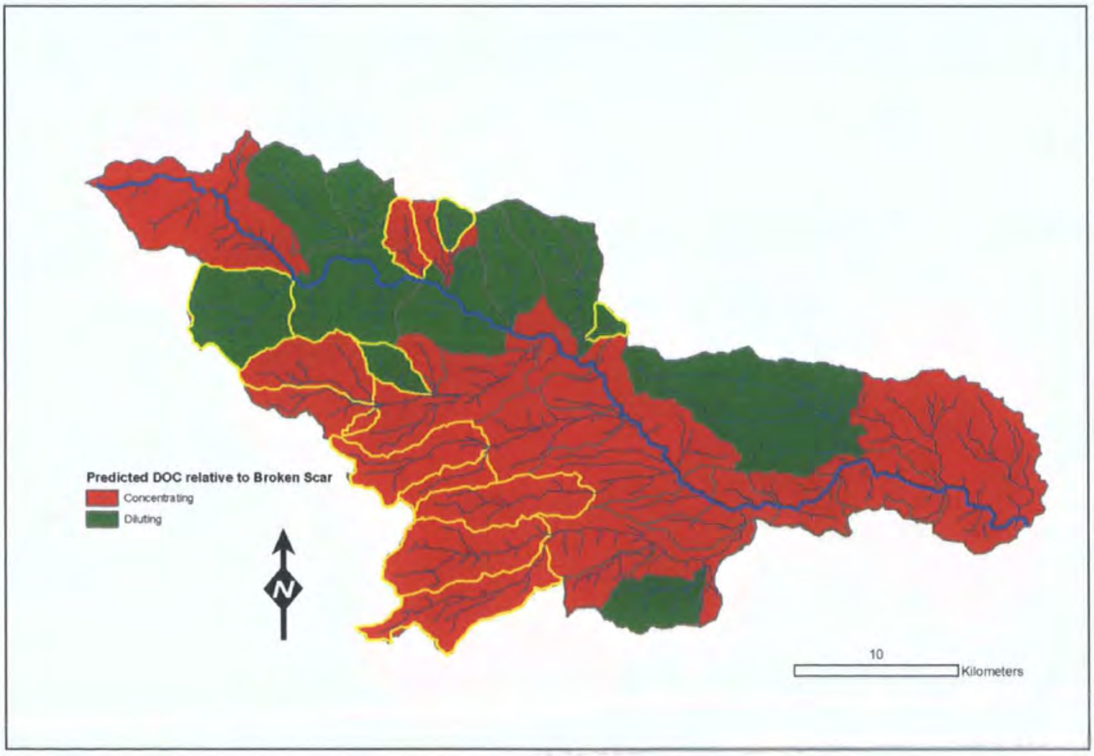


Figure 4.19 Predicted relative DOC concentration for all surveyed sites, with new sites highlighted.

The model can also be applied to the 1km^2 cells in order to generate maps of predicted contributing areas (Figure 4.21). However a conceptual difficulty arises in applying this model to the lowland areas of the catchment where there is no peat cover or gripped areas due to the FP_{ungrip} variable – in these areas FP_{ungrip} = 0 conventionally (with 0/0 = 0) and so the model above predicts all but the steepest such areas to be DOC-concentrating. Furthermore if there is a small amount of peat registered in the soil cover data (due principally to LCM class 5 which occurs in small lowland areas and in reality probably does not represent peat soil) but no grips, then FP_{ungrip} = 1. However the area is still registered as contributing if the mean slope is less than 2.8 degrees ((38.09-30.83) / 1.17), which is true in the flat agricultural lower reaches of the catchment. The model was derived on subcatchments which all (with the exception of Langley Beck) contained a substantial portion of peat cover and therefore the problem did not arise in the development of the model or its application to subcatchments, but this is not the case for all of the 1km^2 cells and the indiscriminate use of the FP_{ungrip} measure is inappropriate in these areas. For this reason, the 1km^2 cells are only allocated as contributing if in addition to being selected by the model, they contain at least 20% peat cover. This value was selected by trial and error to provide a plausible map of the areas which would not be expected to contribute, and also corresponded well to the areas which contained no gripping. The areas which were excluded from being selected as contributing are illustrated in Figure 4.20 and the resultant map of predicted contributing areas is shown in Figure 4.21. This once again suggests DOC contribution to be concentrated in the headwater areas of the Lune, Balder and (to a slightly lesser extent) the Greta, with some small areas in the north of the catchment also predicted to contribute, such as around Crook Burn.

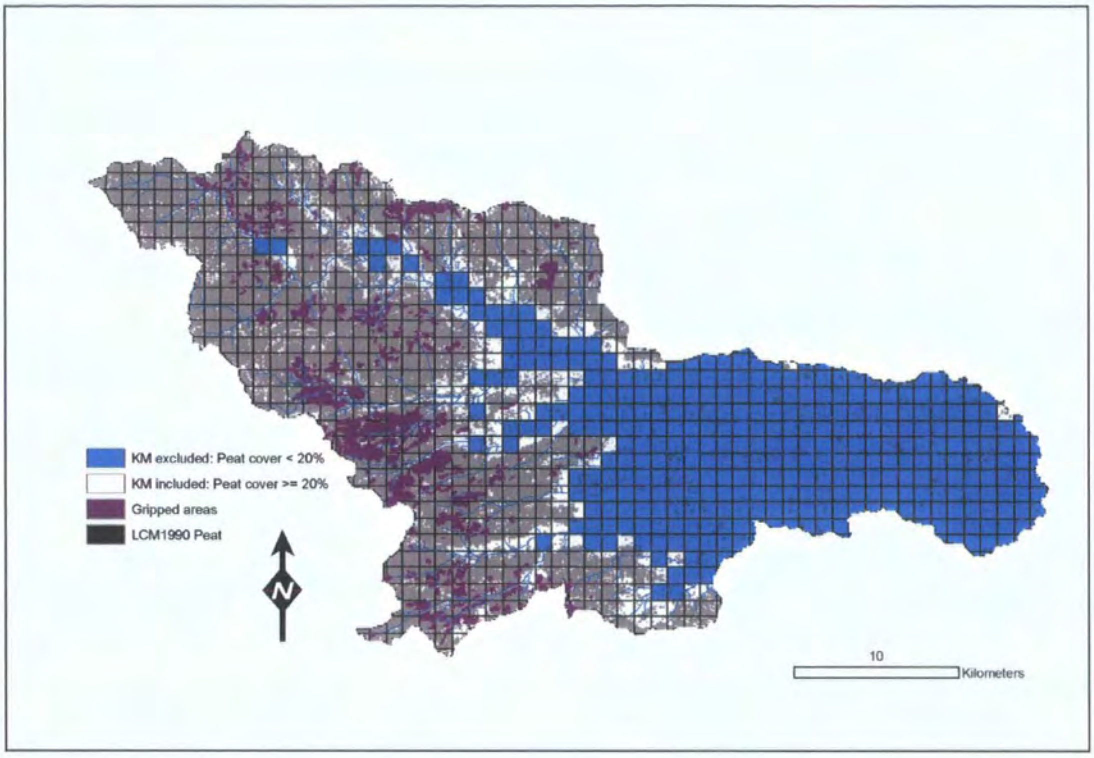


Figure 4.20 Areas excluded (in blue) from the 1km predicted contribution model due to spurious FP_{ungrip} values

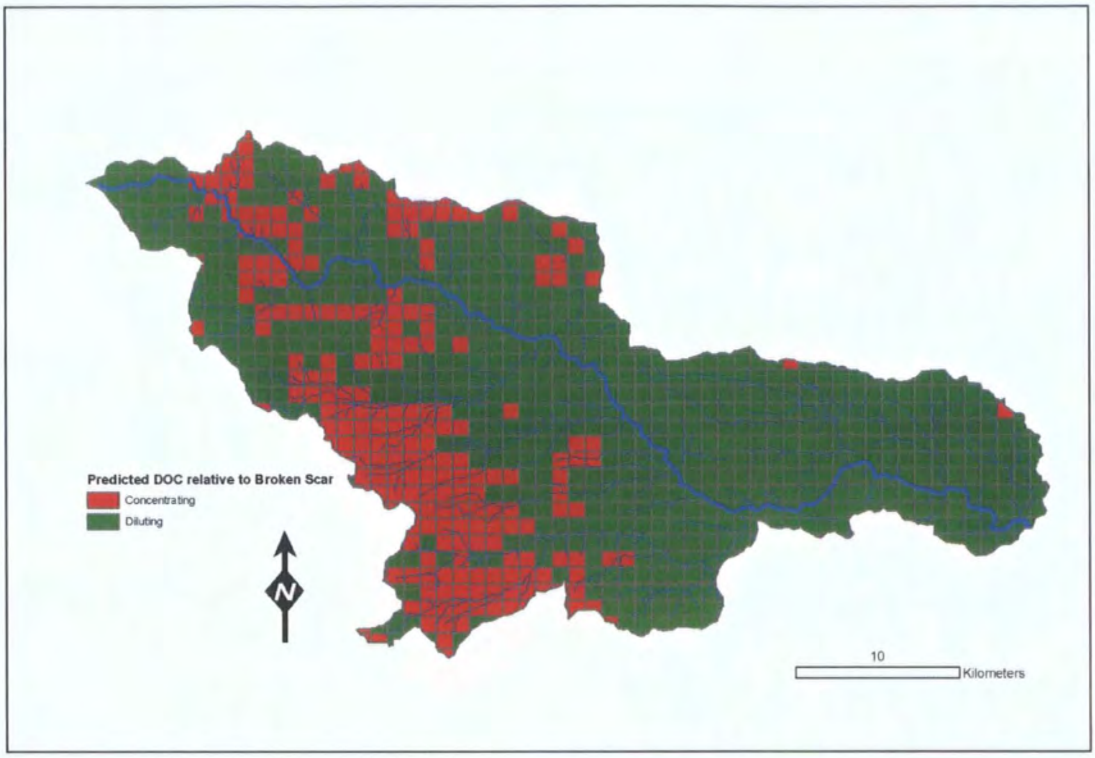


Figure 4.21 Relative DOC contribution predicted for 1km^2 squares from the preliminary model

4.8 Development of the classical predictive models

As described in section 4.6, the modelling work was developed further after the first three sampling runs and production of the preliminary model. It was found that the original strategy of developing the model based on the first three sampling runs and validating it on data from subsequent runs was not entirely appropriate. The relationships between predictor variables and DOC concentrations varied between runs, possibly due to variations in flow conditions across the runs. This meant that one single model could not be expected to predict DOC response successfully, if calibrated on data collected under one flow regime and then used to predict data that was observed under a different flow regime. Ideally many more sampling runs would be conducted to average out the effect of varying flow conditions between the calibration and observation datasets. However this was not possible within the scope of this study where there were not enough sampling runs across a sufficiently wide range of flow conditions to be able to average the data in a meaningful way, and so instead the sampling runs were regrouped taking account of the differing flow conditions prevailing at the time of sampling in order to increase the reliability of the model. In order to select the best grouping, similarities between the runs were identified based on two factors: the actual prevailing conditions at the time of sampling (section 4.8.3.1) and the patterns of correlation of variables with DOC (section 4.8.3.2)

Furthermore, at the time the preliminary model was developed after the first three sampling runs, not all of the catchment statistics shown in Table 4.5 - Table 4.8 had been obtained. In the development of the preliminary model, variables were selected for inclusion manually based on the observed correlation with DOC concentrations in order to develop a best fit model. With the greater number of catchment statistics subsequently derived, a more rigorous and involved approach was required to the selection of potential predictor variables, as the ratio of potential predictor variables to observations was too high for the reliable use of variable selection procedures on the whole variable set. The variable set was therefore manually reduced by interpretation of the variables before passing to the best-subsets algorithm. This was achieved in two ways: firstly by analysis of the correlation structure of the dataset (section 4.8.4), and secondly by manual interpretation of the nature of the variables (section 4.8.5) A new version of the binary logistic regression model was also produced based on the same variable selection strategies (section 4.8.7)

4.8.1 DOC concentrations from the sampling runs

DOC concentrations from each sampling run are summarised in the boxplot in Figure 4.22. The upper and lower box boundaries mark the 75th and 25th percentiles respectively and the centre line represents the median. Interquartile range (IQR) is defined as the difference between the 75th and 25th percentiles. Whiskers extend to the most extreme values which fall within the upper and lower adjacent ranges, which are defined as (75th percentile + 1.5*IQR) and (25th percentile – 1.5* IQR) respectively. All points outside the adjacent range are plotted individually.

It can be seen on the boxplot (Figure 4.22) that the DOC concentrations and the range over which they are spread varied substantially between runs. From the distribution of the concentrations alone, this did not appear to be related strongly to the weather and flow concentrations at the time of sampling, with sample runs 2 and 4 for example taking place under wet and dry conditions respectively, yet showing a similar distribution of sample concentrations. In order to reduce the effect of this variation between the runs as far as possible, the main response variable examined in this study was normalised DOC, obtained by ratioing sample concentration to the concentration observed at the catchment outlet (Broken Scar) on that day. The distribution of this DOC_{norm} variable across sampling runs is shown in Figure 4.23. The outlier points on the plot are in Run 3, the Lune, and in Run 5, Rennygill Sike.

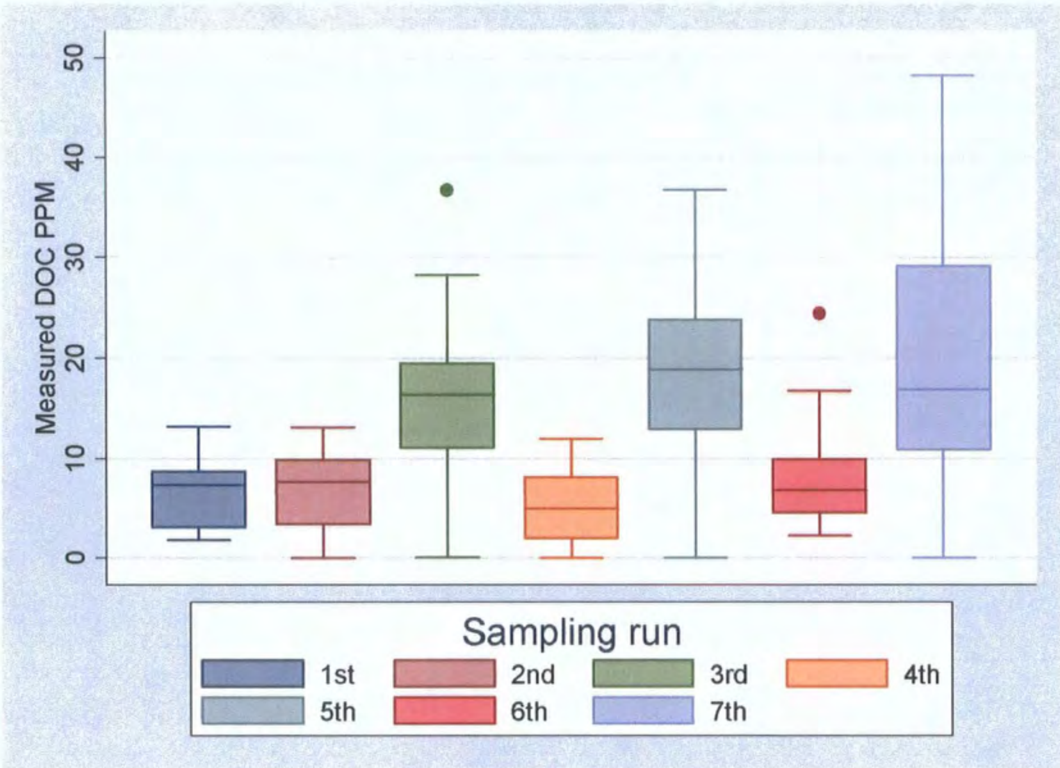


Figure 4.22 Distribution of observed DOC concentration by sampling run

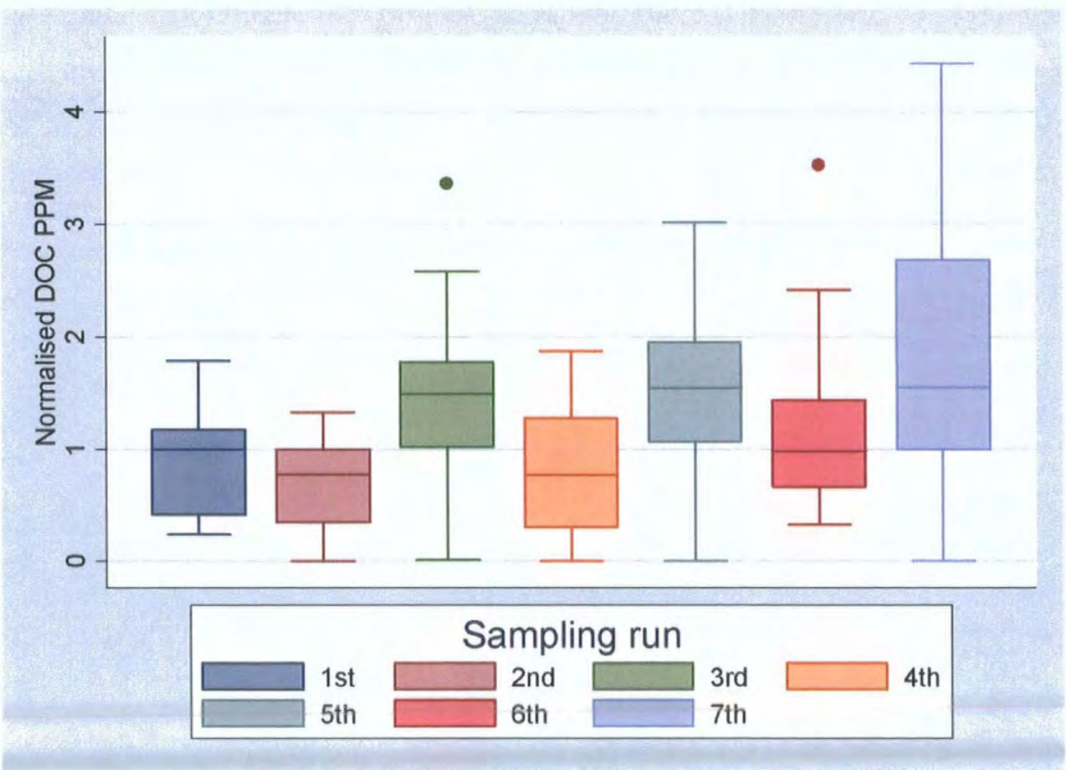


Figure 4.23 Distribution of DOC concentration normalised to Broken Scar, by sampling run. This data was used, averaged across runs, for the modelling work

4.8.2 Correlation of catchment characteristics with DOC concentration

The methods described in section 4.5.2 assist in the elimination of unnecessary variables from the model in order to cope with problems such as collinearity between variables. However they cannot be used blindly on the entire dataset as presented in Table 4.5 - Table 4.8 because relative to the number of observations for each model, there are too many variables. A simple analysis based on the correlation of individual variables with the observed DOC concentrations is therefore conducted first to eliminate those variables which have no significant effect and can be safely discarded in the identification of regression fits for individual sampling runs.

All of the variables described in Table 4.5 - Table 4.8, with the exception of minimum slope (0 in all cases) and all but the most recent grazing intensity, were correlated against normalised DOC concentration for each run individually. Variables significantly correlated ($p < 0.05$) with the normalised DOC concentration for each run are reported in Table 4.10. The set of variables that were found to be significantly correlated with normalised DOC varied between runs, and no one variable was significantly correlated with normalised DOC concentration in every sampling run. The number of variables found to be significantly correlated with DOC concentration varied from four (for the fourth run) to 40 (for the second run).

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Area		0.53					
$Burnt_{frac}$			0.57		0.56	0.74	0.59
$Burnt_{area}$		0.57					
$Gripped_{frac}$			0.54		0.61	0.67	0.70
$Gripped_{area}$		0.58					
$Peat_{frac}$			0.55		0.52		0.58
$Peat_{area}$		0.55					
$Slope_{max}$					-0.50		
$Slope_{range}$					-0.50		
$Slope_{mean}$	-0.52	-0.56		-0.41	-0.74	-0.69	-0.58
$Slope_{std}$					-0.54	-0.73	-0.54
$Elev_{min}$							0.55
$Elev_{max}$		0.48			-0.53		
$Elev_{range}$		0.52			-0.60		-0.51
$Elev_{mean}$			0.39				
$Elev_{std}$		0.43			-0.67	-0.51	-0.57
$Sheep_{88}$			-0.52				
Strahler	0.46	0.44					
Shreve		0.53					
Longestflow	0.43	0.58					
$Stream_{gradient}$	-0.49	-0.48					
$Stream_{length}$		0.53					
$Stream_{density}$						0.66	
FP_{ungrip}	-0.43	-0.48	-0.50		-0.55	-0.65	-0.66
Firstorders		0.53					
Secondorders		0.53					
Thirdorders		0.53					
$Drainage_{intensity}$		-0.53					
$Basin_{length}$	0.43	0.58					
Elongation	-0.47	-0.56					
Perimeter	0.42	0.57					
Crenulation	0.49	0.60					
$Relief_{ratio}$	-0.54	-0.56					
$Relative_{relief}$		0.55					
$A3_{deg}$		0.50					
$\%A3_{deg}$		0.45			0.59	0.55	
$A5_{deg}$		0.52					
$\%A5_{deg}$	0.50	0.56			0.76	0.69	0.59
CLA3		0.51					
TCLA3		0.39			0.53	0.49	
CLA5		0.53					
TCLA5	0.50	0.57		0.46	0.66	0.63	0.54
$Length_{overlandflow}$		-0.40				-0.62	

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Aspect	-0.57	-0.49		-0.40	-0.69	-0.61	-0.51
$Geometry_{num}$		0.53					
LTM_{band3}		-0.48					
LTM_{band4}		0.44			-0.55		-0.60
$LTM_{band3eq}$		-0.50					
$LTM_{band4eq}$							
$LTM_{lcband7}$	-0.49	-0.43		0.45	-0.56		
$LTM_{lcband4}$					-0.51		-0.60
$LTM_{lcband2}$					-0.70	-0.64	-0.66
LTM_{WOUK3}			-0.44		-0.68	-0.56	-0.56

Table 4.10 Correlation coefficients with normalised DOC for variables significantly ($p<0.05$) correlated with normalised DOC for each run

Fraction of peat that is ungripped is significantly ($P<0.05$) correlated with normalised DOC concentration for all the sampling runs except run 4, and mean slope is also significantly ($P<0.05$) correlated in six of the seven runs (excluding run 3). Burnt fraction and gripped fraction were each significantly correlated in all three of the originally-selected validation runs (5-7) but not in either of the first two calibration runs. Correlation with measures of stream and basin characteristics was largely confined to the calibration runs and little significant correlation was observed with any of these variables in the validation runs. The calibration runs included more samples taken from large nested subcatchments along the River Tees itself, compared with the validation runs which included more samples from lower order separate subcatchments.

Results from the second sampling run were significantly correlated with a very high proportion of the input variables, while results from the fourth run were only correlated with at the 5% level with mean slope, TCLA5, aspect, and LTM-LC Band 7. A greater number and variety of sites were sampled in run 4 than any other run and since the weather conditions were dry throughout the run the lack of correlation with the predictor variables in this run may indicate behavioural differences between some of the catchments that were not picked up by the sampling pattern in any of the other runs. Alternatively, the dry conditions may mean that the samples in this run contained relatively little surface or near surface runoff (which is where DOC would be expected to be produced) and so no relationships between these surface variables and DOC concentrations would be expected, as effectively only groundwater was being measured. The measured (as opposed to normalised) DOC concentrations were the lowest in run 4, (Figure 4.22) lending weight to this second hypothesis. In either case, a case can be made for excluding results from run 4 from the analysis, either because the sampling pattern was different with some sites sampled in run 4 and not in any other runs; or because run 4 sampled groundwaters whose DOC would not be expected to respond to surface variables such as soil cover.

4.8.3 Strategies for grouping sample runs

4.8.3.1 Flow conditions

Efforts were made to ensure that sampling runs took place during periods of dry weather, so that streams were as far as possible under baseflow conditions in order to improve replicability. Due to the flashy nature of the hydrograph from the catchments studied, it would otherwise be difficult to ensure that samples were taken at the same point on the hydrographs. However for the second and third sampling runs, the weather changed during the day, and there was significant rain on both these occasions. Total rainfall at Moor House (at the top of the study catchments) on each sampling day and the previous day is shown in Table 4.11.

Sampling run	*Rain in preceding 48 hours*	*Rain during sampling*
1: 4th June 2003	0.2	0.2
2: 30th June 2003	0	4.6
3: 19th November 2003	27.6	0
4: 9th June 2004	0	0
5: 7th December 2004	5.4	0.2
6: 2nd March 2005	7	1.6
7: 28th September 2005	0	0

Table 4.11 Rainfall in mm at Moor House prior to and during each sampling run

Daily mean flow data for the River Tees was obtained from the Environment Agency gauging station at Broken Scar. Mean daily flows around the sampling days are shown in Figure 4.24.

The first sampling run took place during an extremely dry period – total rain at the Cow Green site was 61.4mm in June 2003. The second run took place at the end of this long dry period and there was rainfall during the sampling run. The different pattern of flow conditions during the second sampling run means that streams sampled earlier in the day were under baseflow, while by the end of the day the streams were in spate. This may mean that the results from this run are less comparable as noise may have been introduced into the data by the variation in flow conditions. Alternatively, since baseflows will be reduced to a minimum following a drought period, it can be argued that this second run is the most representative of surface and near surface waters and therefore of DOC production. As long as DOC sources did not become exhausted within the sampling day, this run may provide the best snapshot of DOC production relatively "uncontaminated" by low-DOC groundwater, and provide the best information on the risk areas for peak DOC production, which is usually observed in such "flush" periods following drought. This is reflected in the different pattern of correlated variables for the second run as compared with the others – a far greater number of variables are apparently correlated with DOC concentration for this run. This may be a spurious effect if the effect of the weather on that day was to introduce "noise" into the DOC concentrations. Alternatively, it may be evidence that surface and near surface runoff – dominating the samples on that day – are the most affected by and the most predictable from the catchment characteristics used in this study. This would be expected as the characteristics used are related to surface observations rather than groundwater factors such as geology type.

Sampling runs 3 and 5 both took place on dry days following rain, and therefore are likely to have been on the falling limbs of the hydrographs (although note that this is not evident in Figure 4.24 which is based on daily data – a larger storm followed run 3 and the run appears to be on the rising limb of this storm, but in reality sampling was before that rain started). Runs 1 and 4 were both preceded by dry periods and were themselves also dry. Runs 6 and 7 were characterised by slight precipitation both prior to and during the runs, but in the case of run 6 this may have been due primarily to snowmelt and the effective distribution of this throughout the catchments is unpredictable.

Based on these data, sampling run 2 is the most likely not to represent baseflow conditions, being the worst affected due to the rain falling during sampling, which combined with the flashy nature of the hydrographs means that streams are not likely to have been sampled under the same flow regime as one another. Although run 3 was preceded (and followed) by heavy rainfall, there was none during sampling and so the subcatchments will all have been sampled after the individual hydrograph peaks. Sampling run 6 took place when the ground throughout the catchments was largely snow covered, and so although the precipitation recorded will be due to snowmelt at the raingauge, the flow conditions and sources cannot be assumed to be the same as other periods of low precipitation. Sampling run 7 was conducted after rainfall monitoring ceased but the weather conditions prior to and during the run were observed to be dry.

Therefore the conclusion from an assessment of the actual flow conditions at the time of sampling is that averaging data from runs 1-3 for the modelled response is not the most appropriate combination, due to the differing flow conditions across these runs. Runs 3 and 5 were similar in terms of the weather and likely hydrograph stage, as were runs 6 and 7.

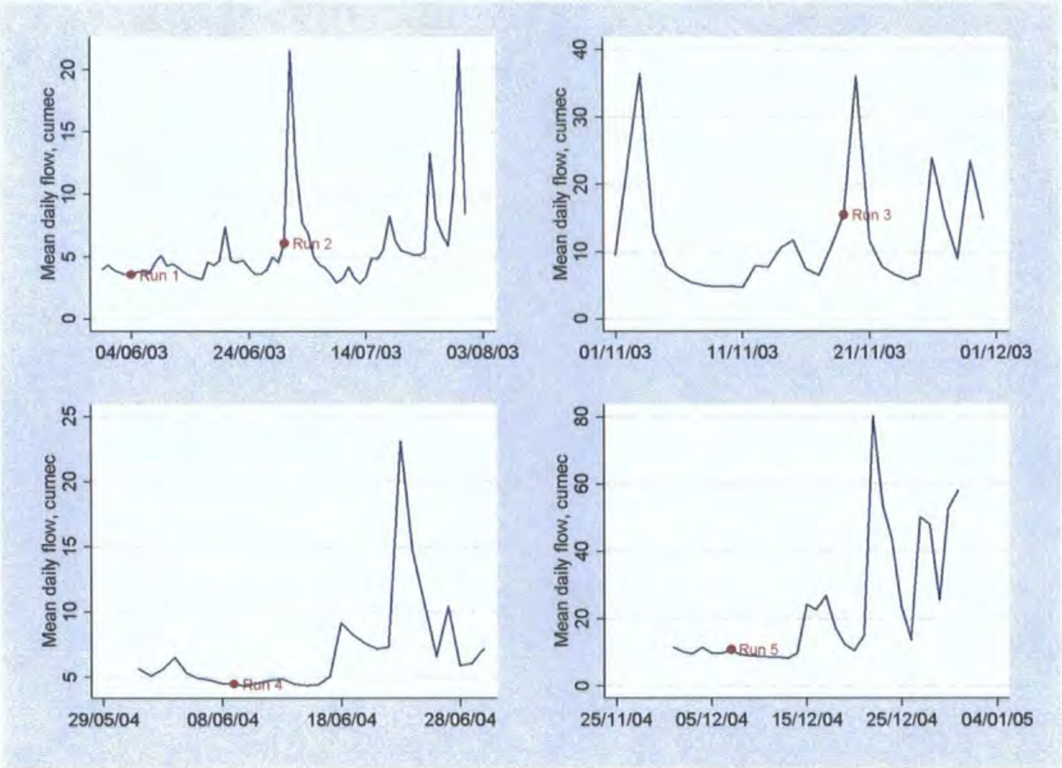


Figure 4.24 Flow in the River Tees at Broken Scar. Note differing scales. Data were not available for 2005 (runs 6 and 7)

4.8.3.2 Cluster analysis of correlated variables

The observations made above on the differences in conditions between sampling runs gave some suggestions as to how the data can be regrouped into calibration and validation sets (section 4.8.3.1). Alternatively, the patterns of correlations between variables and normalised DOC concentration can be examined to look for similarities between the runs that may suggest the catchments were exhibiting similar behaviours. One common technique for finding groupings in such a data set is cluster analysis.

Most cluster analysis methods are based on a measure of dissimilarity, and groups are defined by levels of dissimilarity – observations falling below a cut-off dissimilarity value from one another are deemed to be similar and therefore to comprise a group. Dendrograms are a type of graph with a tree structure allowing the groupings implied by the dissimilarity measure to be visualised. Kaufman and Rousseeuw (1990) provide a comprehensive introduction to cluster analysis. There are many possible dissimilarity measures - a common one is simply Euclidean distance and Kaufman and Rousseeuw (1990) suggest that this is a robust and broadly-applicable method.

To examine the grouping of sampling runs a cluster analysis was performed based on the correlation of variables with normalised DOC concentration in each case (Table 4.10). Each sampling run was taken as an observation, and the correlations of each variable with normalised DOC were taken as the variables for the cluster analysis. An average linkage clustering method was used with the dissimilarity measure being the Euclidean distance. The results of this analysis (Figure 4.25) largely support the grouping of the sampling runs suggested above from observation of the weather conditions, with the largest dissimilarity being between runs 1, 2, 4 and runs 3, 5, 6, 7. The position of run 4 may be unreliable as run 4 was only found to be correlated to four variables and so the cluster grouping is based on minimal input.

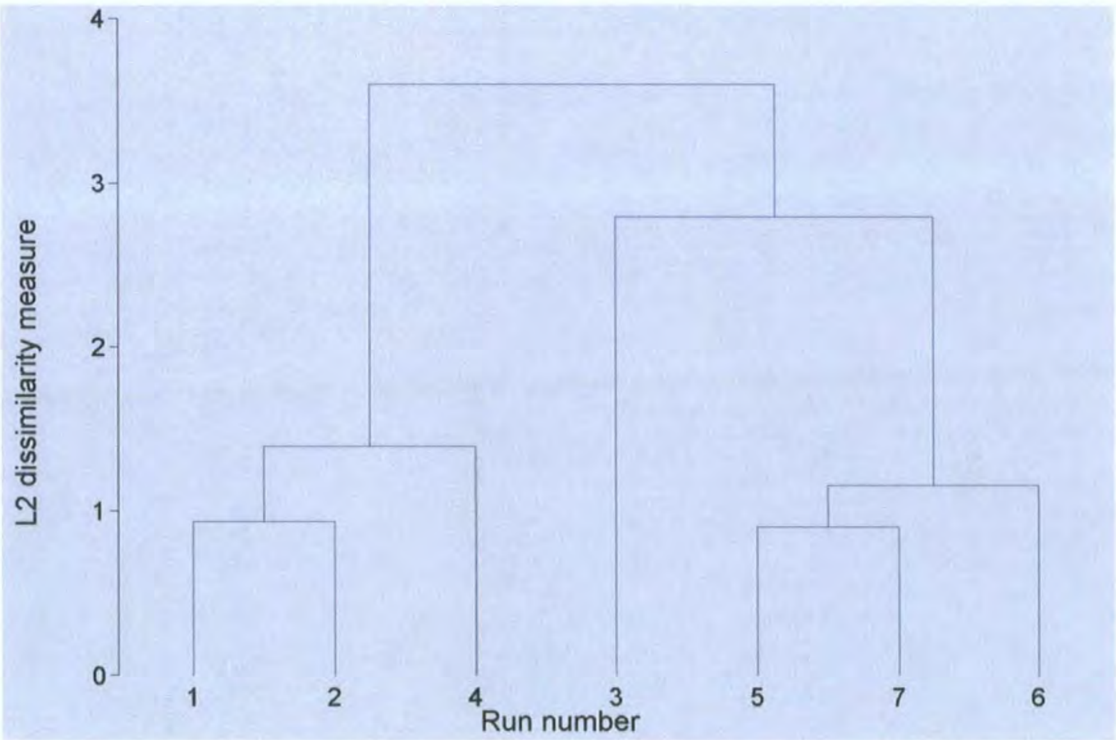


Figure 4.25 Dendrogram from cluster analysis to group sampling runs

4.8.3.3 Overall choice of grouping

Based on the measures of similarity in the previous two sections, sample runs 3 and 5 were considered to be similar, and were therefore grouped together as calibration runs and runs 6 – 7, also considered to be similar, were used as model validation runs. Sampling run 4 was the run which was conducted, as originally intended, under extremely low baseflow conditions, but the results were in fact not observed to be strongly related to the catchment statistics, in comparison to all the other runs.

For the various groupings of runs selected, the response variable was the average normalised DOC concentration for each catchment across each time it was sampled in that group of runs. For instance, in runs 3-5, catchment FP11 (Balder at Cotherstone) was sampled on all three occasions and so the response for this catchment in this group is the mean normalised DOC concentration from these three samples. In the same three runs, catchment FP14 (Little Eggles Hope) was only sampled twice and so the response for this catchment is the mean normalised DOC concentration from these two samples.

4.8.4 Multiple Linear Regression (MLR) models: initial variable set selected by correlation analysis

Beginning with variables that were found to be significantly correlated with normalised DOC in several runs, various combinations of variables were tried as input to the best-subsets regression procedure. (N.B. this was used in preference to the stepwise procedure for the reasons outlined in section 4.5.2.1; however both techniques provided models that were identical for a given size, although the best-subsets procedure sometimes found a better model of smaller size than that identified by the stepwise procedure).

Following the method used for the development of the preliminary model (4.7.2) first, all variables significantly correlated with DOC concentration in any of the runs (3 and 5) were entered into the procedure: 22 variables in total (Table 4.10). Slope range was excluded as it has a correlation coefficient of 1.0 with slope max, because all catchments in fact have a slope min value of 0.

Models were selected based on R^2_{adj}, Mallows C-p, and RMSE. In some cases several models of a given size had almost identical goodness-of-fit statistics and in these cases the model to retain was selected for maximum consistency – for instance the variables gripped fraction and FP_{ungrip} were never selected for the same model, but two models differing only in which of these two variables was chosen were effectively indistinguishable, and in such cases the models were chosen to be as consistent as possible such that the 3 variable model was a subset of the 4 variable model.

The size of model to retain was chiefly a pragmatic decision based on the desire to find a simple yet highly significant model, but this was backed up by analysis of the the goodness-of-fit statistics with increasing model size, which indicated 4 or 5 variables as the best model size (Figure 4.26). As the model size increases further the corresponding improvement in RMSE and Mallows C-p is much less, whilst the chance that the model is overfit increases.

For this procedure the best models for each of 3, 4, and 5 variables (in terms of highest R^2_{adj}, lowest Mallows C-p and RMSE) were as shown in Table 4.12. All variables were significant ($p<0.01$) in all of the models.

Each of these models was used to predict DOC concentrations for the two validation runs (runs 6 and 7). The results of this are shown in Figure 4.27. Predictive ability for the validation runs was marginally best for the 5-variable model but this was only very slightly higher than the 3-variable model, which bearing in mind the danger of overfitting may therefore be the better choice.

n variables	Variables	R^2_{adj}	Mallows C-p	RMSE	Prediction of runs 6-7
3	Peat fraction Frac peat ungripped %A3deg	0.646	7.7	0.407	$R^2 = 0.704$ RMSE = 0.542
4	Peat fraction Slope mean Slope std Frac peat ungripped	0.669	6.4	0.394	$R^2 = 0.644$ RMSE = 0.595
5	Peat fraction Frac peat ungripped %A5deg TCLA5 LTM Band 4	0.694	5.1	0.378	$R^2 = 0.707$ RMSE = 0.540

Table 4.12 Best 3 – 5-variable models for calibration runs 3 & 5 from initial variable set of all variables significantly correlated to response

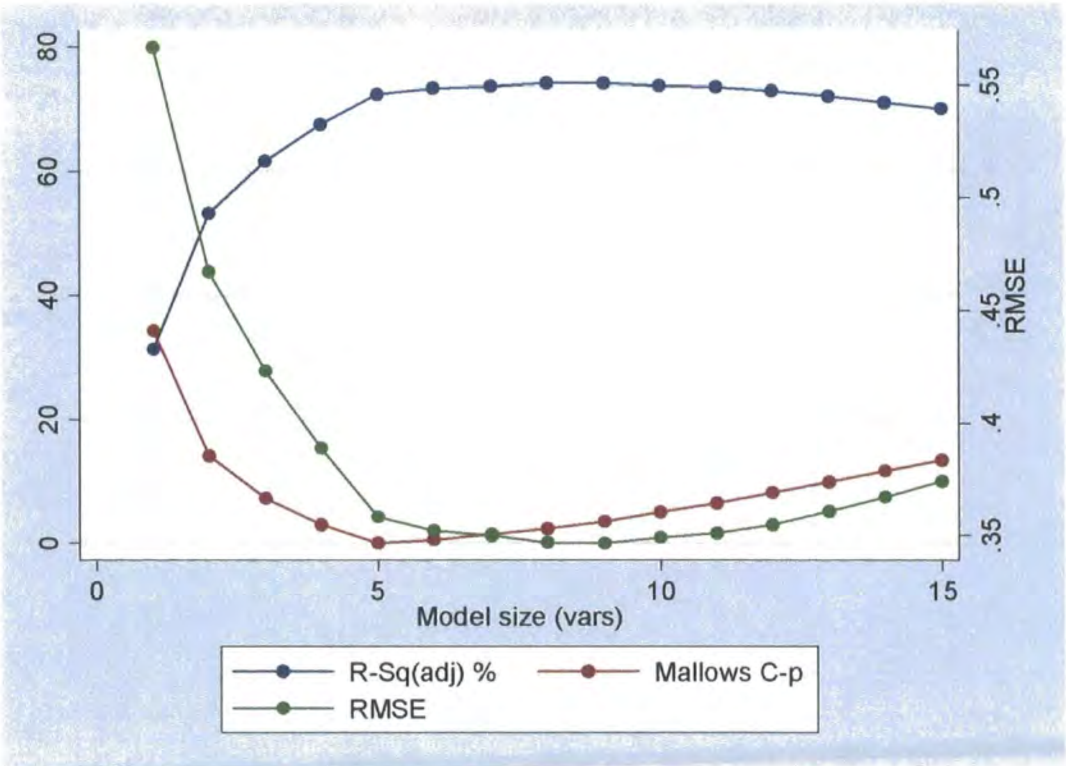


Figure 4.26 Mean goodness-of-fit for the three best models of each size

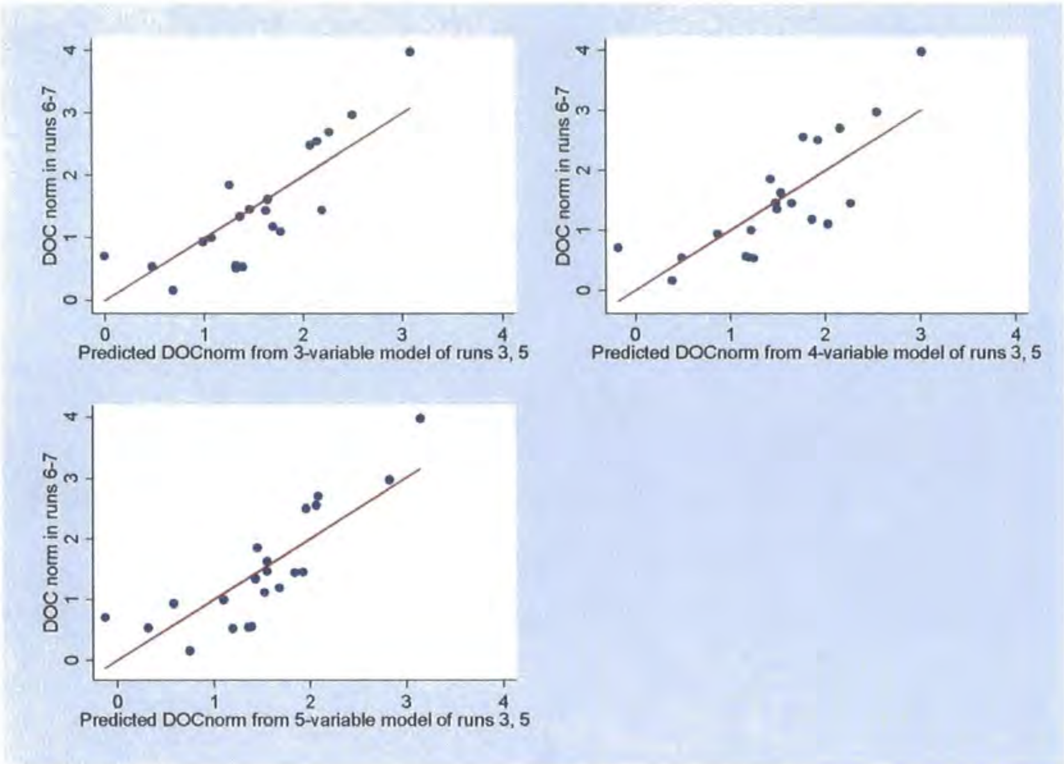


Figure 4.27 Models from runs 3-5 compared to results from runs 6-7. y=x line superimposed for reference.

The pattern of selection of variables by the best subsets procedure shows good correspondence to what would be expected from the preliminary modelling and from understanding of the likely catchment processes. Almost all suggested models include mean slope as a predictor, and some measure of the peat extent and the extent to which it is gripped. As the number of variables increases, a measure of elevation is included (either maximum elevation or relief) and one of the Landsat variables. Whether the gripping variable selected is Gripped fraction or FP_{ungrip} varies, due to the high correlation of these variables when combined with overall peat fraction and the unreliability of variable selection methods in these circumstances. However this also means that the results of the model are not greatly different whether Peat fraction + Gripped fraction, or Peat fraction + FP_{ungrip} are selected.

This suggests that the main processes identified in the preliminary model are also observed in this stage of modelling: low slope, high peat content, high levels of drainage, and (to a lesser extent) high elevation being key factors in increased DOC export.

4.8.5 MLR models: initial variable set selected manually

It is notable that few of the new candidate predictor variables developed for this stage of the modelling were selected for inclusion into the models by the correlation analysis, and in particular none of the measures of drainage density were found to be correlated with the observed data and so were not included in the above models by the automatic and semiautomatic methods described above. Therefore as an alternative, a completely manual prune of the whole variable set was conducted, to select variables based only on prior knowledge of which ones may plausibly affect DOC export. Variables were chosen also in an attempt to minimise the selection of those which would be affected by the nested nature of the catchments (such variables would include maximum elevation, and maximum slope) in order to reduce the effect of this nesting and maximise the extent to which the catchments could be considered separately. Variables were selected as described below:

Burnt fraction and gripped fraction were each selected as both burning and gripping are known to affect the hydrological behaviour of the peat in addition to increasing the potential oxidation and DOC production within the peat, as described in chapter 1. Overall peat fraction was also included as peat is taken *a priori* to be the chief source of colour. Catchment area was included because in combination with any of these percentage variables, the overall area of those landcover types can be derived and there is therefore no need to include burnt area, gripped area, and peat area separately. Mean slope was included because it has been found in all stages of the modelling and in several other studies to be an important indicator of potential DOC production, and the reasons for this are understood. No other slope variables were included as these are considered somewhat spurious – maximum slope could take on an extremely high value, not reflecting the nature of the catchment, if two adjacent DTM cells spanned a crag or some other relief feature, while minimum slope is in all cases 0 or close to it. It is not clear which of the elevation variables is the most relevant to include, given the reasoning in section 4.7.2, although mean elevation seems the most likely to provide a true effect rather than some collinear effect with another variable. Of all the grazing years measured the most recent was used. This variable is measured on a spatially more coarse scale (parishes) than any other and so its use may be limited – this scale is coarser even than the 1km^2 resolution HOST dataset. Furthermore it is likely that it will represent collinearities with other variables as upland regions such as peat bogs provide lower quality grazing and have lower grazing intensities, whilst also exporting more colour due to the peat content. Therefore the inclusion of this variable into the model should be interpreted with caution and would warrant further research to produce a more detailed dataset of grazing intensity.

Of the drainage morphology variables, four were selected to represent the best possible range of the likely underlying effects: drainage intensity, percentage area below 5 degree slope, total channel length in these areas, and length of overland flow. Variables such as the number of first order streams and total channel length are correlated with area due to the nested nature of the catchments and so the variable Drainage Intensity was selected instead to represent the overall level of drainage in the catchment. Hortonian Length of Overland Flow represents the average length of the flowpath for a rain droplet before reaching a stream channel, and was included based on the idea that colour is transferred into water as it passes through soil (rather than in the streams) and so a greater average length of overland flow may be related in some way to colour. Mean aspect was included based on the observed relationship in the preliminary modelling between colour levels and northern / southern catchments. However, this variable will not necessarily provide any extra information as to the cause of this trend: it has been observed that the northern catchments in this study are generally steeper and somewhat lower in peat cover than the southern ones. To identify whether there is an underlying cause behind the trend would require monitoring of a greater range of catchments to the north and south.

With these caveats, the regression procedure was repeated with these manually selected variables. The quality of the fit with increasing model size followed a similar pattern to previously, as illustrated in Figure 4.28 for the three best models of each size. The best model of each size was selected and is described in Table 4.13. The best 3 variable model was not greatly different from those in the previous procedure (Table 4.12) but the models of 4 or more variables included one or more of the manually-added variables. The R^2 fit of the model to the data from the calibration was not greatly different but the Mallows C-p value was improved for the four and five variable models. Furthermore the prediction of the results from the validation runs was notably improved for the four-variable model (Figure 4.29).

n variables	*Variables*	*R^2_{adj}*	*Mallows C-p*	*RMSE*	*Prediction of runs 6-7*
3	**Peat frac** **Frac peat ungripped** **%A5deg**	**0.627**	**6.3**	**0.418**	**R^2 = 0.706** **RMSE = 0.540**
4	**Peat fraction** **FP ungrip** **Slope** **Drainage intensity**	**0.669**	**3.6**	**0.394**	**R^2 = 0.776** **RMSE = 0.472**
5	**Peat frac** **FP ungrip** **%A5** **Drainage intensity** **Band 4**	**0.737**	**-1.1**	**0.350**	**R^2 = 0.738** **RMSE = 0.510**
6	**Peat frac** **FP ungrip** **%A5** **TCLA5** **Drainage intensity** **Band 4**	**0.731**	**0.7**	**0.354**	**R^2 = 0.742** **RMSE = 0.507**

Table 4.13 Best 3-6 variable models for validation runs 3&5 from manually trimmed variable set

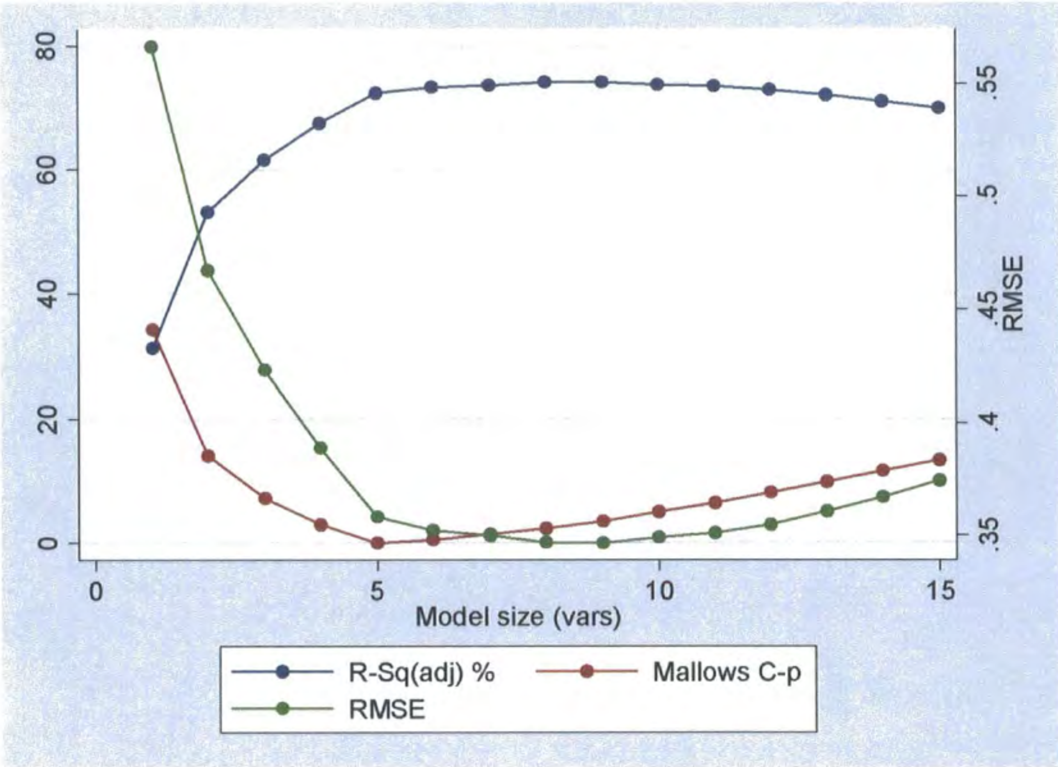


Figure 4.28 Mean goodness-of-fit for the three best models of each size derived from manual variable selection

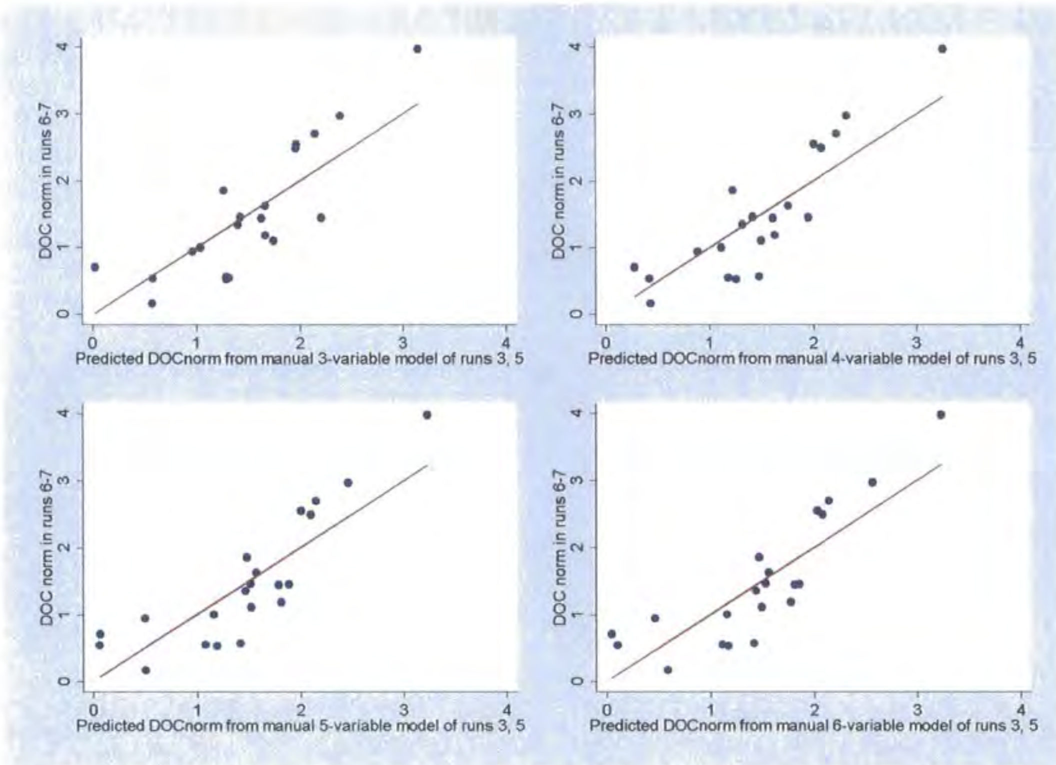


Figure 4.29 Models of runs 3 and 5 derived from manually selected variables, used to predict results of runs 6 - 7

4.8.6 MLR models: final model selection

Due to the improved Mallows C-p and prediction of validation data, the four variable model developed from the manually-pruned variable set was selected from the models described in Table 4.12 and Table 4.13 as being the best model for prediction of DOC export from catchment characteristics. The full details of this model are as follows

$$DOC_{norm} = 1.649 + 2.09 Peat_{frac} - 1.995 FP_{ungrip} - 0.263 Slope_{mean} + 0.535 Drainage_{intensity}$$
$$R^2 = 0.708 \quad R^2_{adj} = 0.669 \quad \text{RMSE} = 0.394 \quad \text{Mallows C-p} = 3.6$$

Equation 4.4 The final predictive regression model. Model was developed from best subsets regression on a manually-selected initial variable set

All variables including the constant are significant with $P < 0.02$ and the model overall is significant with $P < 0.0001$.

Applying this model to 1km squares (Figure 4.30) shows a different distribution of concentrations compared to the preliminary model (Figure 4.13). Particularly notable are the higher extreme values predicted by this new model, of up to seven times higher than Broken Scar. This is not unexpected given the high concentrations observed in catchments such as Rennygill Sike that were not included in the data for the preliminary model. The less visually distinct distribution into high / low concentration areas, relative to the preliminary map, is also partially due to the different scales used on these two maps; an equal-interval classification would reduce this but given the differences in high extreme values between the models, would not be appropriate. Also notable is the wider range of values in the lower (eastern) half of the catchment, with a few squares such as one at the northern edge of the Langley Beck catchment having particularly high predicted values that seem unlikely.

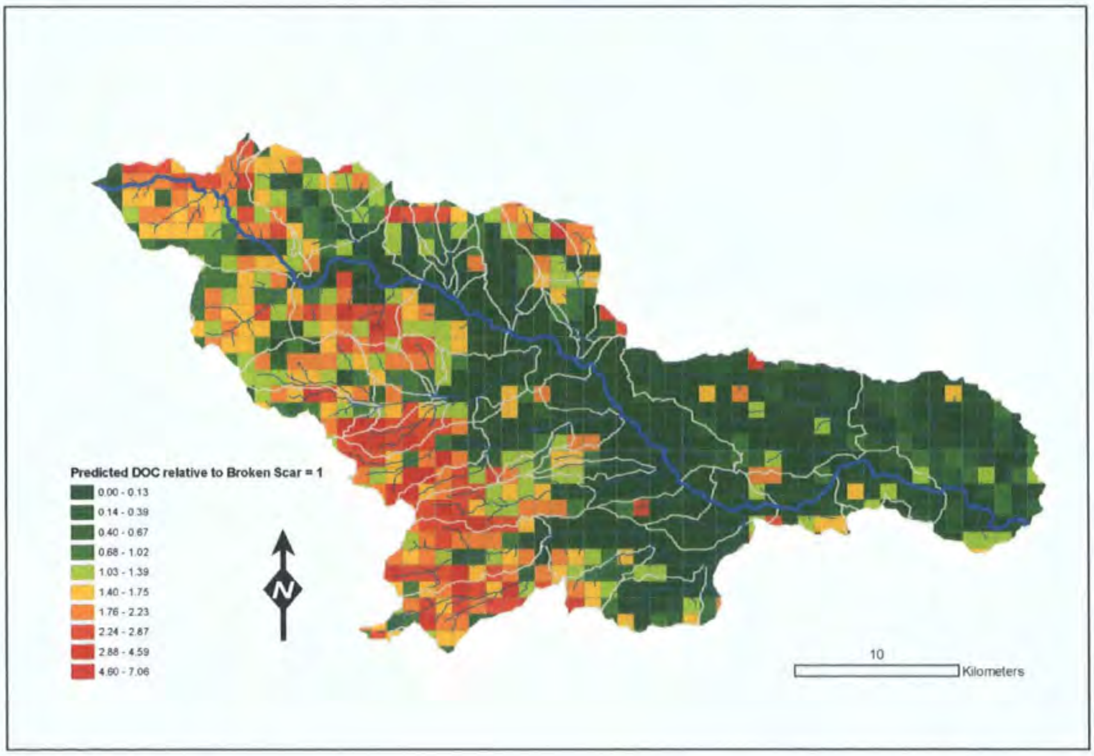


Figure 4.30 Final multiple linear regression model, applied to 1km squares

4.8.7 Binary logistic regression models: final model selection

The binary logistic regression procedure was also repeated in order to take account of the new potential predictor variables and on the new calibration vs.

validation datasets. As in the development of the preliminary model, the stepwise logistic regression procedure could not be run on all of the correlated variables that were taken as input to the multiple linear regression procedure, as the model proved to be unstable due to the small number of observations and correlations between the input variables. Therefore the modelling procedure was run iteratively several times with different combinations of potential variables until a stable model was found (the final model selected was identified separately from several different sets of input variables). The best fit logistic regression equation was then given by

$$\ln\left(\frac{\theta}{1-\theta}\right) = 3.55 + 15.45 Peat_{frac} - 0.06 LTM3_{equalisedmean} - 31.71 Length_{overlandflow}$$

Equation 4.5 Final logistic regression model, developed by stepwise selection of variables from a manually-pruned initial set

With a cut-value of Θ = 0.5, this model predicts a site to be contributing where the inequality is met:

$$3.55 > 0.06 LTM3_{equalisedmean} + 31.71 Length_{overlandflow} - 15.45 Peat_{frac}$$

Equation 4.6 Final logistic regression model, expressed as an inequality for identification of DOC-contributing sites

The model shows 87% concordance with the data, with 8/12 negative outcomes and 25/26 positive outcomes correctly predicted, and all variables are significant at the 95% level. Application of the model to 1km squares is shown in Figure 4.31 – as the FP_{ungrip} variable was not included this model was not restricted like the preliminary model, but very few areas that were restricted from the preliminary model were identified as contributing by this final model. This model identifies far more areas as contributing compared to the preliminary model, in particular the catchments of Maize Beck and the Tees above Cauldron Snout.

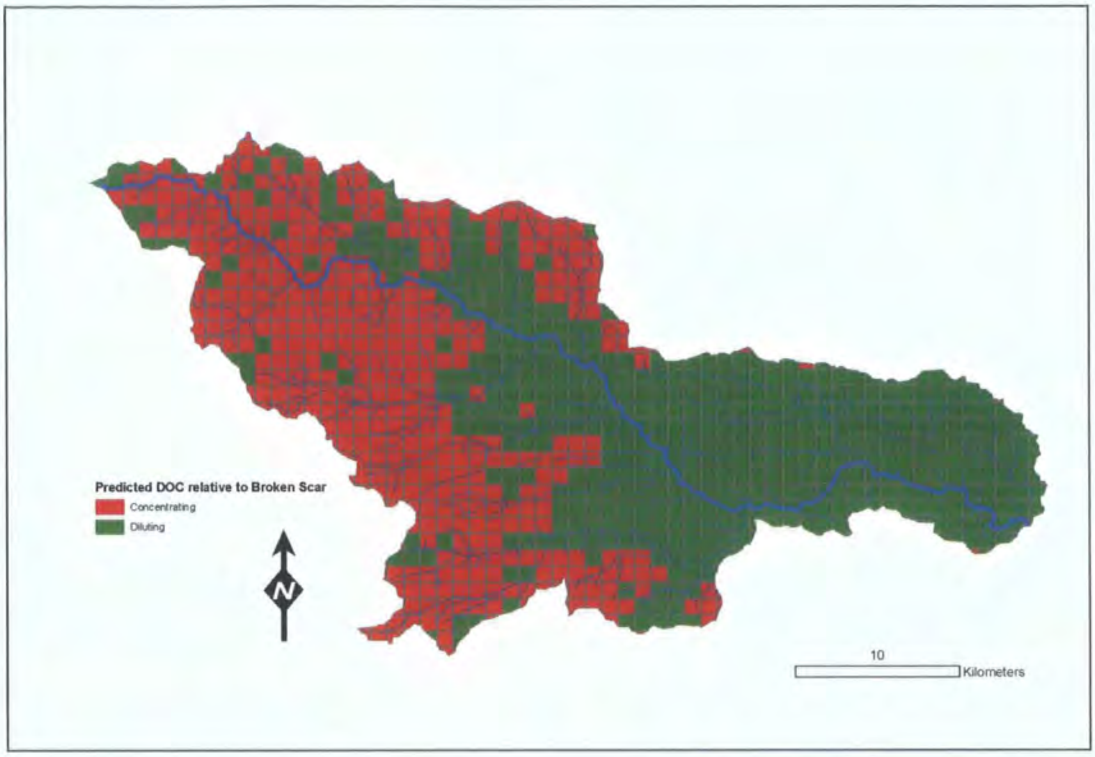


Figure 4.31 Final logistic regression model applied to 1km squares

This model incorporates two variables that were not available during the development of the preliminary model: the histogram-equalised version of the LTM Band 3 data, and the Hortonian length of overland flow. The ability of the model to predict the outcome is however not greatly higher than the preliminary model, and any difference may reflect the more realistic grouping of the data, taking into account flow conditions, resulting in a less noisy dataset.

To demonstrate this, modelling the preliminary dataset with the same variables used in the final model: $LTM3_{eqmean}$ $Length_{overlandflow}$ and $Peat_{frac}$, results in a similar (77.8%) concordance with the data as did the preliminary model, and the $Length_{overlandflow}$ term is not significant in the model at the $p < 0.05$ level.

Conversely modelling this final dataset with the two variables used in the preliminary model, $Slope_{mean}$ and FP_{ungrip}, results in a slightly worse (77%) concordance with the data, but only the $Slope_{mean}$ term is significant. The conclusion is that both models fit their calibration data with a very similar quality of fit (85% for the preliminary model on runs 1-3; 87% for the validation model on runs 3-5), and also predict the other dataset with a very similar fit (77% for the preliminary model on the validation dataset; 78% for the validation model on the preliminary dataset).

4.9 Discussion of the classical predictive models

Although the individual models produced have varied, there have been firm similarities between them, and this modelling has shown that DOC export concentration, and whether or not a site contributes to overall DOC concentration, can be predicted with some success from a small set of catchment characteristics. The study does not include enough data, in particular lacking a seasonal analysis, to identify one particular variable over another. For example FP_{ungrip} is included in the preliminary model; peat fraction is included in the validation model. However this also suggests that exactly which variable is used is not so important, due precisely to the cross-correlation between them, yet DOC export and therefore whether a site contributes colour overall to the downstream WTW can be accurately predicted given information about a small number of underlying catchment trends. This suggests that the fact that many of the studies described in section 4.2.1 used different catchment descriptors in developing relationships between catchment characteristics and DOC or colour export need not imply that the results of those studies, and the present one, cannot be compared.

Slope of the catchment is perhaps the most important and readily understood of these variable trends. Mean slope is included in the preliminary model and length of overland flow, included in the validation model, is more correlated with mean slope than with any other variable (Pearson correlation coefficient 0.49, $p < 0.0000$). Slope is a fundamental characteristic of a catchment and many other catchment characteristics are related to it; for instance peat accumulates only in areas of relatively low slope. Low slope also results, all other things being equal, in slower surface runoff and less direct runoff pathways, and therefore greater opportunity for DOC to be transferred into runoff water.

Nevertheless, there is of course not a complete correlation between slope and peat cover, and so some measure of peat cover is also important along with slope in predicting DOC export. Peat is taken *a priori* in this study to be the key source material for DOC, and the results of the modelling back this view. The modelling has also shown that the treatment of the peat affects the runoff colour, with more drainage leading to more DOC in the runoff. This corresponds with the results found in chapter 2 and chapter 3, which identified much higher DOC export from the grip sites than from natural, pristine, streams. This part of the study does not incorporate data on the extent to which the drained areas are blocked; nor is the density of drainage considered. This means that quantitative relationships to predict the expected change in riverine DOC fluxes cannot be derived for this catchment. However, the presence of drainage as a significant variable in these models does suggest that any decrease in export from individual drains would scale up in a signifiant way to the riverine DOC levels. It should also be noted that burnt areas were also associated significantly with DOC runoff, but because burnt and gripped areas are largely similar throughout the catchments in this study the data do not allow the relative effects of the two treatments to be clearly distinguished.

Elevation also plays a role in the predictive models but it is unclear from the data whether this is fundamental and separate from land cover type, or whether this is a consequence of the higher peat cover in higher catchments. A greater range of catchments would be required including lowland peat catchments and upland catchments with lower peat cover in order to test whether the effect of elevation itself is relevant.

4.10 Partial least squares regression

4.10.1 The need for an alternative technique

The stepwise and best-subsets regression procedures address the problem of collinearity in the predictor variables by selecting a limited subset of these variables. However, the selection procedures are guided only by preselection of the variables significantly correlated with the response variables, they do not by definition select only predictor variables that are uncorrelated with one another. Therefore where two or more predictor variables are correlated with one another and also with the response variable, the stepwise or best-subsets procedure does not address this and can still encounter problems such as unstable model coefficients. Furthermore some argue that not only is the number of observations required for a classical regression analysis higher than is often appreciated (Green, 1991), variable reduction techniques such as stepwise regression do not reduce this requirement as may be assumed from the smaller resultant model size. For example, Babyak (2004) showed that the number of observations that is required to run a stepwise procedure is higher than is often appreciated: the number of degrees of freedom used in the variable selection remains dependent on the number of variables in the initial set, not in the final model. This implies that although variable selection methods produce a smaller final model, the number of observations required to justify this is not reduced.

For these reasons Judd and McClelland (1989) make three key objections to the use of stepwise and best-subsets algorithms: Firstly, that they will not necessarily produce the best model where there are redundant predictors. Secondly, although best-subsets methods will identify the best model of each size, the fact that smaller models are not necessarily subsets of larger ones presents a serious conceptual difficulty. Thirdly, stepwise methods have a disproportionately large chance of fitting peculiarities of a particular dataset (Judd and McClelland, 1989; also see discussion available at http://www.pitt.edu/~wpilib/statfaq/regrfaq.html). The implication of this is that in such cases the models may be unstable, in terms of which one of several potential highly correlated predictor variables are selected.

In the present study, this was illustrated by the inconsistent choice of variables and their coefficients between the models. Although reasonable fits were achieved in each case, and the models produced can therefore be used to predict DOC concentration with some success, a regression equation such as is produced by the models implies an explanatory effect on the modelled variable. However as the models varied in terms of which ones of several collinear variables were selected, they cannot justifiably be said to fully *explain* the data. If one model includes gripped fraction and another includes peat fraction, it is impossible to say which of these variables "explains" the corresponding trend in DOC concentration. From the datasets as collected, predictive models may be successfully produced but it is harder to draw firm conclusions about the explanatory effect of *individual* variables, where those variables are correlated in the modelled dataset but not necessarily in the overall population. For example, slope and drainage density may be substantially correlated in one set of catchments, but this does not imply that they are correlated in all cases. It would then be impossible to determine, from the sample data, which of the variables was responsible for the modelled effect.

Therefore although models such as those produced in this study may well be of use in the prediction of DOC export, in order to be considered statistically justifiable an alternative approach or verification is required. The variables selected in the various models in sections 4.7 and 4.8 were of several common themes, as discussed in section 4.9, which argues for the use of decomposition methods to represent the underlying trends in the predictors before regression. These themes (factors or components) will not only be more appropriate for use to predict DOC concentration, but analysis of the contribution of the variables to the components will allow better understanding of the underlying explanations (an aspect that will be addressed in chapter 5). PLS presents one such possible solution; its use for modelling DOC export is demonstrated in this section.

4.10.2 Background to the PLS regression method

The PLS method works by relating the weights for components between the predictors and response(s), rather than relating the predictors and responses directly (Section 4.5.2.3). In order to use the resulting model for regression and to predict new responses, the coefficients must therefore be extracted in terms of the original predictors, not their scores or weights in the model. This procedure is most clearly explained in terms of matrices, as follows (description adapted from Statsoft, 2003):

With constant and error terms excluded, the multiple linear regression model $\boldsymbol{y = b_1x_1 + \ldots + b_nx_n}$ can be written in matrix form as **Y = XB** where **Y** is the response matrix (a vector if there is only one response), X is the matrix of predictor variables (one column for each variable) and **B** is the coefficient matrix (a vector if there is only one response).

In order to use the fitted PLS model in the same way as the multiple linear regression model, the coefficient matrix **B** must therefore be derived, transformed back to the original scales. To do this the component extraction first computes the weights for each component (the eigenvectors) which form a matrix **W** with one column for each component and one row for each variable. This is the actual component analysis stage of the procedure, where the component eigenvectors **W** are produced to take into account the covariance between the predictors and the response(s) (in the case of principal components analysis, **W** would be extracted based only on the correlation or covariance of the predictors).

Component scores are then calculated as **T = XW**. Next the loadings for the Y variables are computed by regressing **Y** on **T** such that **Y = TQ** where **Q** is the matrix of loadings for the response(s) (error terms are once again omitted in this explanation). This can now be expanded to give the coefficients for predicting Y in terms of the original predictors:

Since **T = XW**, we can rewrite **Y = TQ** as **Y = XWQ**. So if **B = WQ**, then **Y = XB**, which is the required prediction model (with constant and error terms once again excluded for clarity), and it can seen that the coefficients of the linear regression model, represented by the matrix **B** which has one column for each response variable and one row for each predictor variable, are derived from the eigenvectors (weights) for the components multiplied by the loading for each response.

In addition to providing the weights, loadings, and scores for the x and y data, the software used (Minitab 14 and XLSTAT) does this work, providing the back-transformed coefficients **B** for the original variables so that the PLS model can be used as a traditional regression equation. The resulting regression equation can be used in the same way as a traditional model, however the number of predictors in the model can be much higher without this meaning that the model is overfit, as the coefficients were derived using the PLS procedure. The procedure is therefore more statistically justifiable for use on limited datasets such as those in the present study.

4.10.3 Results of the PLS regression modelling

Partial Least Squares regression models were produced in Minitab 14 and XLSTAT. The number of components to retain was selected in Minitab using a cross-validation procedure to maximise the predictive ability of the model on its own calibration dataset. The PLS regression procedure was run several times with one response variable each time. The response variable was, in turn, the DOC concentration normalised to Broken Scar and averaged for runs 1-3, runs 3-5, runs 3 and 5, and all runs. All the gathered predictor variables (Table 4.5 - Table 4.8) were initially entered into the procedure. The cross-validation method was used to select the number of components to retain in the model by maximising the predicted R^2 on the cross-validation data. The model resulting from the back-transformed regression coefficients was used to predict normalised DOC concentrations for each site in the same way as the multiple linear regression models, and these were compared to the observed normalised concentrations for various combinations of runs to assess the predictive ability of the models.

The data included some outlier points, in particular Rennygill Sike, resulting in misleadingly high R^2 values for prediction. Although the Rennygill Sike data are not believed to be erroneous, the catchment is quite different to all the others, being a first-order stream with peat cover close to 100%. The hydrological behaviour of the catchment may therefore be different (compare the different behaviours of the grips and the larger streams, in chapter 3). To address this, the models were analysed primarily in terms of RMSE which is less affected by outliers (note the differing values in the two R^2 for prediction of Runs 6-7 columns, compared to the more similar values in the two RMSE columns). The modelling was also repeated excluding Rennygill Sike due to the high leverage of this data point, but this made less difference (compare the two Runs 3-5 model rows). This itself points towards the greater robustness of the PLS technique to the outliers or fluctuations that are to be expected in a small dataset such as this.

Models were assessed for their fit to the calibration data and also the fit to the validation dataset of runs 6-7. The validation dataset was also assessed with Rennygill Sike excluded. A summary of the fit of each of these models is shown in Table 4.14. The fraction of variance in the predictor variables that is represented in the components is also shown.

Calibration dataset for model	*Number of components selected by cross-validation*	*Fraction of variance in predictor variables represented by components*	*R^2 of model*	*R^2 pred of model*	*Prediction of data from runs 6-7*		*Prediction of data from runs 6-7, Rennygill Sike outlier point excluded*	
					R^2	*RMSE*	*R^2*	*RMSE*
Runs 3,4,5 All sites	3	0.692	0.638	0.322	0.524	0.687	0.315	0.686
Runs 1,2,3 All sites	2	0.572	0.629	0.124	0.538	0.678	0.310	0.688
Runs 3,5 All sites	3	0.684	0.663	0.295	0.672	0.571	0.520	0.574
Runs 3,4,5 Rennygill excluded	3	0.678	0.578	0.078	0.497	0.707	0.325	0.681
Runs 1,2,3 Rennygill excluded	2	0.572	0.629	0.124	0.538	0.678	0.310	0.688
Runs 3,5 Rennygill excluded	3	0.668	0.659	0.247	0.699	0.548	0.542	0.561
All runs All sites	3	0.691	0.716	0.399	0.784	0.464	0.672	0.475
All runs All sites, Rennygill Sike excluded	2	0.601	0.488	0.187	0.771	0.477	0.707	0.448

Table 4.14 Fit of each tested PLS model. The model selected is highlighted.

For similar reasons to the earlier regression procedures, the best calibration dataset was found to be the mean of runs 3 and 5, with the model produced from this data offering the best fit both in terms of the degree to which the model explained the observed data and to which the model predicted new data.

The model selected by cross validation based on this response data retained three components, which represented 66.8% of the variance in the original predictor set. It should be repeated that (unlike in PCR) the components in PLS are selected in order to maximise the extent to which they predict the response variable(s); the implication of this is that only the aspects of the predictor data which are useful to explain the response data will be represented in the components and particularly those components which are retained. A model which predicts the response data very accurately may nonetheless represent a lower proportion of the variance in the original predictor data, if some predictors are not of use for prediction of the response.

The X-loadings for the three components in the model are shown in Table 4.15. These represent the extent to which each variable contributes to each component. Loadings of greater than ±0.180 are highlighted in red and green respectively for ease of visual interpretation (this is an arbitrarily selected value that was found to provide good contrast – it does not imply that 0.180 is any particularly significant cut value).

Due to the number of variables the components are complex to interpret and as discussed previously analysis of the structure of the components (for explanatory purposes) is not the key aim of PLS regression. Nonetheless from the point of view of the key patterns in catchment characteristics which affect DOC export, it can be seen that the components do separate in a basic way. Component 1 loads negatively on many variables that are closely linked to the size of the catchments: Area, Area of several cover types, stream order, length of longest stream, etc. Meanwhile the component loads positively on the three key proportional variables Burnt fraction, Gripped fraction, and Peat fraction. Component 2 is positively loaded on many of the variables closely linked to the size of the catchment that are negatively loaded in Component 1, partially cancelling out the effect of these in the overall model, whilst the proportional variables represented in Component 1 are not strongly represented in Component 2. The effect of these two components together could be seen as modelling a portion of the variance in the catchment-size variables whilst at the same time showing that they are not intrinsically strongly linked to the response, whereas the fraction of the catchments that is peat covered, gripped or burnt is linked to the response. Component 3 is weighted towards the physical aspects of the catchment including slope (as Slope mean, %A3deg, %A5deg, TCLA3, and TCLA5) and elevation, suggesting that such variables do have an effect that is separate from variables such as peat cover fraction, even though they are strongly correlated. Together these results can therefore be taken to agree with the pattern suggested earlier that the key themes in the predictor data which are relevant to the exported DOC are firstly, the extent of peat cover and the extent to which this is gripped or burnt, and secondly the overall steepness of the catchment.

Variable	*PLS Component 1*	*PLS Component 2*	*PLS Component 3*
Area	0.256	0.192	0.025
$Burnt_{frac}$	0.227	0.063	-0.003
$Burnt_{area}$	-0.232	0.200	0.031
$Gripped_{frac}$	0.223	0.052	0.119
$Gripped_{area}$	0.238	0.200	0.038
$Peat_{frac}$	0.289	0.004	0.282
$Peat_{area}$	-0.249	0.196	0.044
$Slope_{min}$	-0.013	-0.081	0.149
$Slope_{max}$	0.242	0.160	0.072
$Slope_{range}$	-0.242	0.160	0.071
$Slope_{mean}$	-0.100	-0.085	0.329
$Slope_{std}$	-0.153	0.075	0.170
$Elev_{min}$	0.254	-0.126	0.182
$Elev_{max}$	-0.185	0.131	0.251
$Elev_{range}$	-0.278	0.165	0.066
$Elev_{mean}$	0.130	-0.041	0.358
$Elev_{std}$	-0.294	0.146	0.072
$Sheep_{88}$	-0.103	-0.016	-0.172
$Sheep_{80}$	0.004	-0.037	-0.075
Strahler	-0.233	0.158	-0.012
Shreve	-0.258	0.192	0.028
Longestflow	-0.253	0.199	-0.010
$Stream_{gradient}$	0.103	-0.182	0.167
$Stream_{length}$	-0.256	0.192	0.024
$Stream_{density}$	-0.032	-0.013	-0.189
FP_{ungrip}	-0.142	-0.065	-0.084
Firstorders	-0.258	0.192	0.028
Secondorders	-0.257	0.192	0.028
Thirdorders	0.256	0.192	0.030
$Stream_{frequency}$	-0.093	-0.045	0.119
$Drainage_{intensity}$	-0.007	-0.037	0.254
$Bifurcation_{ratio}$	0.004	0.037	0.051
$Basin_{length}$	-0.252	0.199	-0.016
Elongation	-0.102	-0.135	0.236
Perimeter	-0.254	0.198	-0.005

Variable	*PLS Component 1*	*PLS Component 2*	*PLS Component 3*
Crenulation	-0.021	0.180	-0.195
$Relief_{ratio}$	0.095	-0.185	0.185
$Relative_{relief}$	-0.273	0.183	0.022
$A3_{deg}$	-0.244	0.187	-0.002
%A3deg	0.063	0.090	-0.346
A5deg	-0.250	0.191	0.009
%A5deg	0.097	0.098	-0.344
CLA3	-0.249	0.189	0.002
TCLA3	0.035	0.077	-0.331
CLA5	-0.253	0.192	0.012
TCLA5	0.064	0.094	-0.329
$Length_{overland\ flow}$	0.071	-0.010	0.175
Aspect	-0.071	-0.115	0.262
$Geometry_{num}$	-0.256	0.192	0.027
LTM_{band3}	0.079	-0.130	0.202
LTM_{band4}	-0.331	0.080	-0.106
$LTM_{band3eq}$	0.136	-0.139	0.181
$LTM_{band4eq}$	-0.157	0.083	-0.187
$LTM_{LCband7}$	-0.046	-0.062	0.304
$LTM_{LCband4}$	-0.281	0.016	-0.150
$LTM_{LCband2}$	-0.339	0.024	0.062
LTM_{WOUK3}	-0.263	-0.062	-0.007

Table 4.15 X-loadings for the selected full PLS model

The model fit the calibration response data with $R^2 = 0.659$ and RMSE = 0.369. Standardised regression coefficients for the model are shown in Figure 4.32; these provide the best indication of the relative importance of the individual variables to observed DOC, according to the PLS model. It is clear that some variables are much more important in the model than others. These largely follow the patterns identified in the earlier modelling procedures and correspond well to the variables that were earlier selected for manual analysis (section 4.8.4), adding confidence to this earlier selection. In particular burnt, gripped, and peat covered fractions are identified as the most important land-use variables, along with mean elevation, relief ratio, length of overland flow, and drainage intensity, and several of the Landsat layers. The procedure did not allocate a very high weight to any one in particular of the variables strongly correlated with mean slope, including mean slope itself, but rather allocated approximately equal weights to several of these variables including mean slope, main stream gradient, $\%A5_{deg}$ and $\%A3_{deg}$. It is therefore clear that slope intrinsically plays a major role in this model, but the overall effect is split by the procedure into several parts.

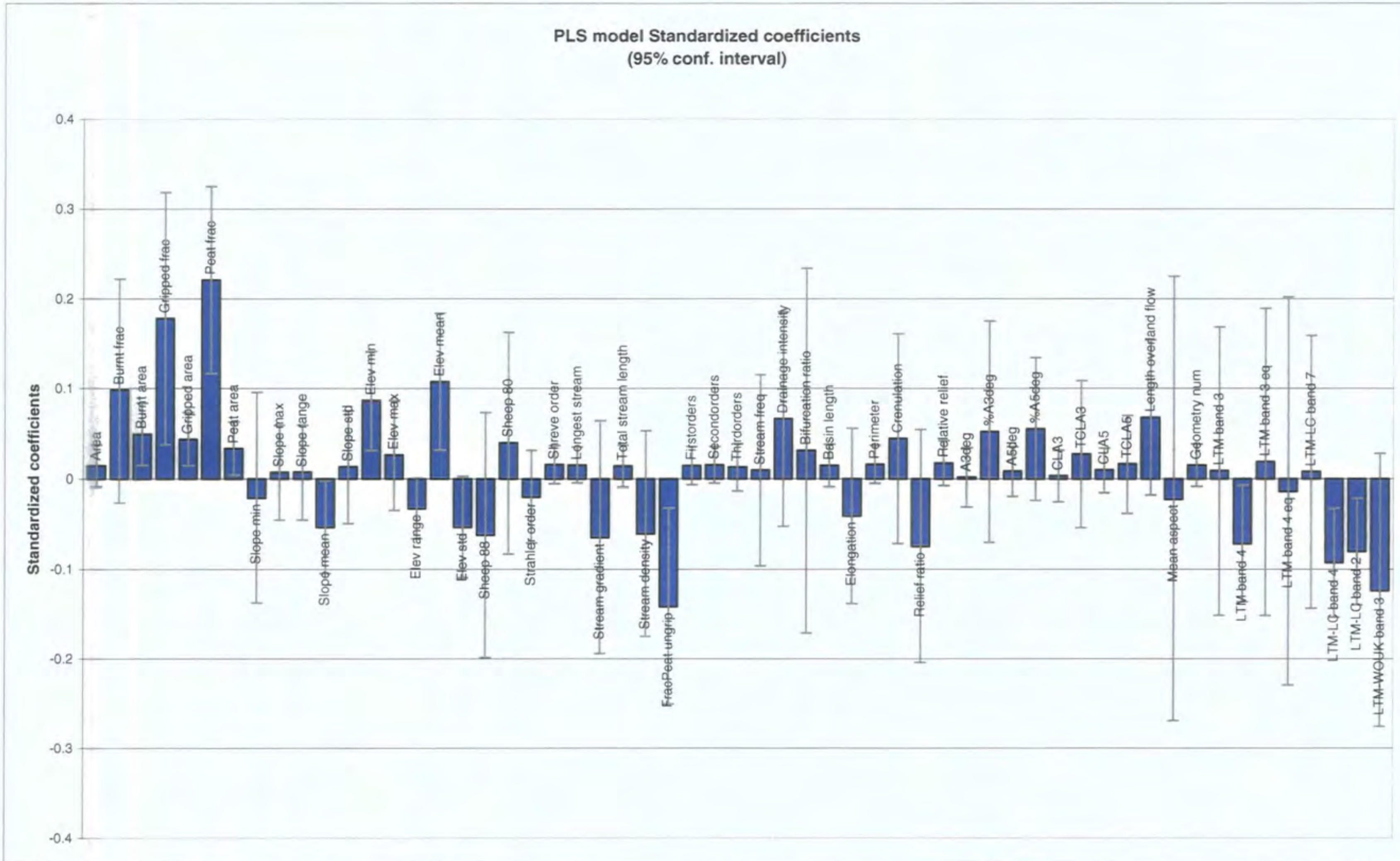


Figure 4.32 Standardised regression coefficients from the PLS model, with 95% confidence limits from the jack-knifing procedure

It should be emphasised again that PLS is primarily a predictive, not an explanatory procedure and therefore we cannot assume from this that the influence of slope can only be modelled usefully by the inclusion of several closely-correlated variables in this manner – it may well be that a single one of these variables would result in a model of very similar quality and, arguably, greater explanatory power. Rather, the use of the model should be seen to be the prediction of DOC concentrations given this entire set of input variables, without extensive analysis of the underlying patterns in the data.

Despite this the PLS procedure has often been criticised (Westad and Martens, 2000), because of the lack of significance testing for individual predictor variables that is inherent in the method. In stepwise linear regression, variables are selected for entry to or removal from the model based on their statistical significance (as described in section 4.5.2.1) – the F-statistic is calculated for the coefficient of each variable to identify the most significant one to add to (or remove from) the model. With the PLS procedure, no such test is available for the significance of individual variables and so no method has been available to guide the selection of variables in order to reduce the model size.

However, it has recently been shown that the PLS procedure *can* nevertheless be extended to enable the model to be developed and honed to use fewer predictor variables. Forina et al (2004) discuss several methods by which this can be achieved and compare them to methods used in conventional regression techniques. The technique discussed here is referred to by Forina et al (2004) as the Martens Uncertainty Test. Initially presented by Martens and Martens (2000), it first develops an estimate of the uncertainty of the regression coefficients, before using this to eliminate variables.

Martens and Martens (2000) suggested a method by which the information produced in the cross-validation procedure can be used to assess the significance of the model coefficients. During the cross-validation procedure, the PLS model is calculated many times, with each time a different selection from the original data being omitted (either one or more observations at a time). The purpose of this is primarily to test the ability of the model to predict the data that has, on that iteration, been omitted, and is implemented in software such as

Minitab to guide the model selection by selecting the model with the number of components that maximises the predicted R^2 achieved by this cross validation procedure. However, each time this procedure is carried out, a slightly different value will be obtained for the model regression coefficients, as the available data for the model at that stage is slightly different. Martens and Martens showed that the range of values thus obtained for each regression coefficient can be used in a conventional manner to estimate the uncertainty and distribution of that coefficient, and thus produce confidence intervals for the regression coefficients. Martens and Martens (2000) and Westad and Martens (2000) went on to show that the information from this can be used to guide the selection or elimination of variables from the model. Any variable for which the 95% confidence interval of the coefficient encompasses zero cannot be said to be significant at this level in the model (Westad and Martens, 2000) as it cannot be said with this level of confidence that the coefficient is different from zero. For the model shown in Figure 4.32 this is the case for many of the variables.

This method is not implemented in the Minitab software and so the data was imported into the XLSTAT software for derivation of the confidence intervals. The XLSTAT model was set to run with the same parameters as the Minitab model, rather than using the internal model selection procedures of XLSTAT, in order to ensure consistency (XLSTAT does not by default use a cross-validation procedure to select models). Figure 4.32 shows as error bars the range on the standardised coefficients representing a 95% confidence interval obtained from this jack-knife procedure.

Of the 57 variables in the original model, only 12 have confidence intervals found by this technique to be significantly different from zero (those with confidence bars that do not cross the x-axis, Figure 4.32). The PLS model was therefore re-run on the same response data with only these twelve predictor variables: $Burnt_{area}$, $Gripped_{frac}$, $Gripped_{area}$, $Peat_{frac}$, $Peat_{area}$, $Slope_{mean}$, $Elev_{min}$, $Elev_{mean}$, FP_{ungrip}, LTM_4, LTM_{LC4}, LTM_{LC2}.

This time the cross validation procedure retained 6 components which explained 95.6% of the variance in the predictor variables – for comparison, a 6 component model with all the predictor variables would have explained 82.9%

of the predictor variance. The model fit the calibration data with R^2 = 68.8% and RMSE = 0.353. This shows that the model much better encapsulates the predictor variance, because the predictors are all more relevant to the response and so will all be included to a greater extent in the selected components.

This PLS model was used to predict DOC values for all sites and the predictions compared to the results from the various combinations of runs, as was the case for the OLS modelling. Applied to 1km squares (Figure 4.33) the model results appear promising, although of course this has not been validated for each such square. Generally, discrimination of key DOC source areas is clearer. Additionally the low predicted concentrations for the lowland eastern areas of the catchment are much less "noisy" with the vast majority of cells falling into the lowest classification on the map; this seems a more likely distribution given the absence of peat soils and drainage in these areas. Again this is an indication of the greater robustness of the PLS technique to outliers: previously PLS was suggested to be more robust to the effect of the Rennygill Sike outlier point in the response data; here it is seen to be more robust against outliers in the predictor data. In this dataset, this is represented by the identification of some lowland areas as peat when in reality the LCM class 5 may not be appropriate throughout (as described in section 4.7.3). Although in this particular case a better approach would of course be to remove this LCM class, the key point is the greater robustness of the technique against such faults.

Conceptually this greater robustness can be described as being due to the greater number of variables in the model; each of which contributes a smaller part to the overall result, minimising the effect of errors in individual variables. However, since PLS is the technique which makes the use of such large models justifiable, this is a key advantage inherent to the technique.

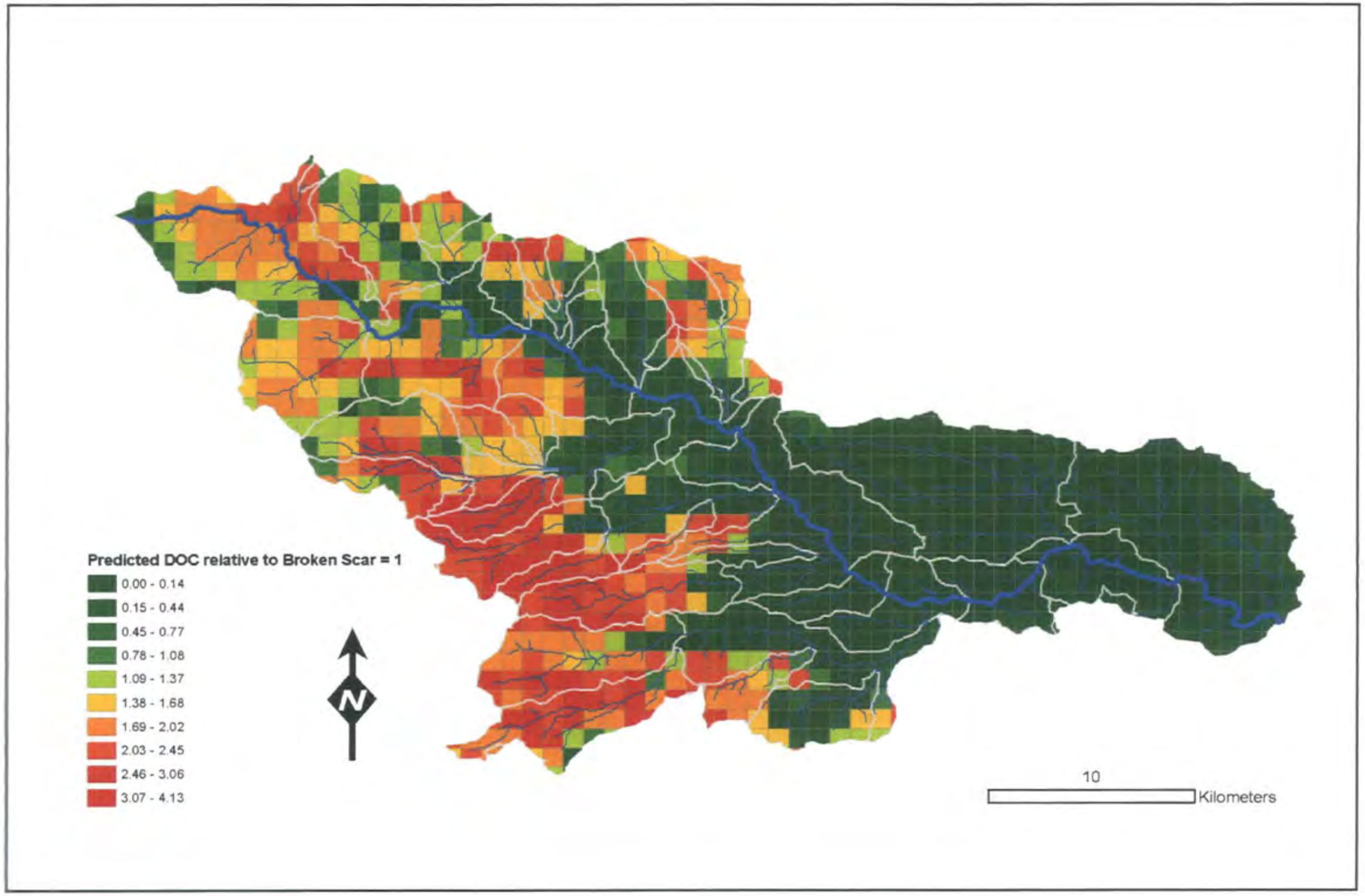


Figure 4.33 Normalised DOC predicted from the 12-variable PLS model for 1km squares

4.11 Summary

This chapter has described a field campaign to monitor DOC concentrations in the runoff from numerous subcatchments of varying size and nature within the catchment of the River Tees above Broken Scar. Following on from the work of Mitchell and McDonald (1995) and others (section 4.2.1) the study has sought to relate the DOC export to catchment spatial and landuse characteristics. The models produced identified peatland management (burning and gripping), in addition to peat cover, elevation, and slope as being the key predictors of increased DOC concentration. These findings are in agreement with the general pattern of those identified in previous studies and the variation in precisely which variables were found to be significant, both in previous studies and this one, has been explained in terms of the limited suitability of the data for classical regression techniques.

However, the present study has extended the work of the above-mentioned studies in the following key ways:

- Derivation of a greater range of catchment characteristics through field surveys, interpretation of third-party datasets, and GIS analysis techniques.

- Representation of observed and modelled fluvial DOC not just as a variable quantity, but alternatively as a binary variable, relating an observed concentration to that at the point of interest at the catchment outlet and representing it either as higher (concentrating) or lower (diluting). Statistical modelling was consequently carried out using binary logistic regression in addition to multiple linear regression techniques in order to identify more deterministically the predicted source areas.

- By providing a review of the use of variable selection techniques in multiple linear regression to identify the catchment characteristics with the largest effect on DOC concentration, and the comparison of these mechanically-identified variables with those identified from expert understanding of catchment behaviour and DOC production.

- Through the use of the emerging technique of PLS regression to generate predictive models of the same datasets. PLS regression is a more robust technique than multiple linear regression, placing fewer requirements on the size and quality of the dataset. The large number of spatial characteristics and the relatively small number of observed DOC concentrations that could be included in a single model, due to variations in flow conditions between sampling runs, meant that the data were not ideally suited to conventional linear regression techniques which was why the variable selection techniques were used. However, these techniques can be somewhat non-deterministic or over-sensitive with such datasets, with two key problems. Firstly, that the model is extremely sensitive to the peculiarities of the dataset used for calibration, and may not be truly extendible, and secondly, that the presentation of a model comprising only a few variables implies an "explanatory" power which may not really be there. (For example a variable closely-correlated to but perhaps more obscure than mean slope may be selected, whilst with a very slightly different input dataset, mean slope itself may be selected. Either case could be seen to imply that the variable selected is in some fundamental way "responsible" for the observed response whereas in fact neither is anything more than a representation of a single underlying effect.)

  The use of PLS regression, which is not subject to the same constraints, was nonetheless found in this study to identify similar combinations of variables to the conventional techniques. This fact adds confidence to the use of the models produced by this study and this suggests that the linear regression-based models of this study and others can be accepted despite the non-ideal nature of the starting datasets. Furthermore since PLS models are produced from latent variables or components, which represent the structure in the original dataset, their use for prediction can be justified without the same caveats about explanatory links between predictors and response.

- The use of an iterative model development process. A preliminary model was developed first after three sampling runs had been completed, and this was used to identify key sites for both high and low DOC contributions. Several such sites were then included in the subsequent sampling studies in order to provide the best possible test of the model.

- Demonstration of the use of GIS systems to apply all these models in a predictive context, to identify key potential DOC source areas. This approach is intended to be of use to various stakeholders in the catchment management process, in particular the water companies or others who are responsible for the consequences of increasing DOC load and who therefore wish to better focus catchment management strategies to decrease the DOC loads observed downstream.

The key drawback of this study was in the size of the usable dataset. It was acknowledged at the outset that the scope of the project did not permit enough sampling to produce meaningful averages across a wide range of flow conditions or seasons and so a decision was made to constrain sampling to a particular flow regime; namely dry conditions, as the flashy nature of the catchments studied precluded sampling of all catchments equally at any other hydrograph stage. However, even this proved difficult to achieve due to the frequency of wet or changeable conditions in upland environments. Furthermore many sites were sampled only on one or two occasions and not necessarily on the same runs or under the same flow conditions. A satisfactory model could therefore not be found to link the results of all the studies, as the behaviour varied between samplings. The data were therefore analysed taking into account the actual conditions that had prevailed at the time of sampling, with data only from those runs that had occurred under similar conditions being included in the models. It is testament to the promise of this modelling work that models of the quality achieved could nevertheless be found, suggesting that DOC export is a highly predictable quantity given a range of readily-obtainable data about the catchment.

Further work should be undertaken to extend the range of the sampling in order to account for the problems described and to consider, for example, the effect of seasonality. Further sampling runs across a full range of flow and seasonal conditions would help with this, but a more robust potential approach for this may lie in the use of rating curves. Given sufficient data from a site it may be possible to develop DOC concentration rating curves to predict DOC export relative to flow and season – for example Cooper and Watts (2002) demonstrated the successful application of the rating curve method to model DOC export for a site in the headwaters of the River Severn.

Given such rating curves for a range of catchments such as those in this study, a PLS regression modelling approach could then be used to seek relationships between spatial catchment characteristics and the rating curve coefficients, with the ultimate aim of robustly predicting the DOC concentration rating curve (rather than spot DOC concentrations) for a catchment based on the spatial characteristics.

5 Identification of sources through mixing analysis and multivariate techniques

5.1 Introduction

Chapter 4 described the results of a sampling campaign that was conducted to monitor DOC from numerous sites across the River Tees catchment, and related these results to spatial characteristics of the source areas using GIS analysis and statistical modelling. This enabled the identification and further prediction of key DOC source areas.

In addition to DOC concentration, the samples collected during these campaigns were also analysed for concentration of several base metal cations. The work in this chapter will use these data to address a different approach to the identification of colour source areas, by assessing the mixing behaviour of the waters in order to identify source areas based on the water samples themselves, rather than on characteristics of the source catchments. Mixing analysis techniques can be used to identify the source of a mixed water relative to a number of end-members (forward modelling), or alternatively to identify potential such end-members from the mixed samples. The multivariate technique of Principal Components Analysis will be used to assess the mixing in this way, using a similar technique to that demonstrated in chapter 3 for grip water samples, but extending the method by considering the spatial distribution of the sources.

5.2 Format of this study

The concept of mixing end members in the Broken Scar catchment was addressed indirectly in chapter 4, in so far as the binary logistic regression approach discussed in that chapter was based on the concept of end members – one end member of "clean", low DOC concentration water and one end member of high-DOC water, with the catchment output at Broken Scar lying between these end members. These end-members applied only to one variable, DOC concentration, and a more sophisticated approach to identifying mixing patterns and therefore colour source areas is available through multivariate modelling techniques. These techniques were described in section 3.4, where they were used to identify differences in behaviour between the peat drain catchments. The techniques allow a statistical approach to mixing analysis: through analysis of the patterns underlying the dataset they allow end members to be identified, and samples to be described in terms of proportions of those end members. They can thus be used to analyse more thoroughly the mixing behaviour of the Broken Scar subcatchments.

Therefore, this chapter presents the results of a multivariate analysis of the behaviour of the Broken Scar catchment and a number of subcatchments, and of the sources and development of the water along the river system. Samples from the campaigns described in chapter 4 were analysed for a suite of other solutes and properties in addition to the DOC analysis described in chapter 4. These results are used in this chapter to conduct a multivariate analysis with the aim of identifying the behaviour of the catchments and the sources, and describing the development of water along the river system. The results of the analyses are analysed spatially, both by consideration of the nested nature of the catchments, and through GIS mapping of the end-member proportions onto catchment maps.

5.2.1 Study sites

This study used the same sampling sites described in chapter 4. These represent a wide range of subcatchments across the river system from first-order streams to the main catchment outlet, across a variety of terrains and land cover types. The catchment map and numbering key is shown in figure 4.2.

Many of the subcatchments examined in this study are nested. This has implications for any mixing analysis as it allows an assessment of the relative contributions of source waters. A schematic map of the catchment nesting structure is shown in Figure 5.1 and Table 5.1 repeats the catchment numbering scheme for reference.

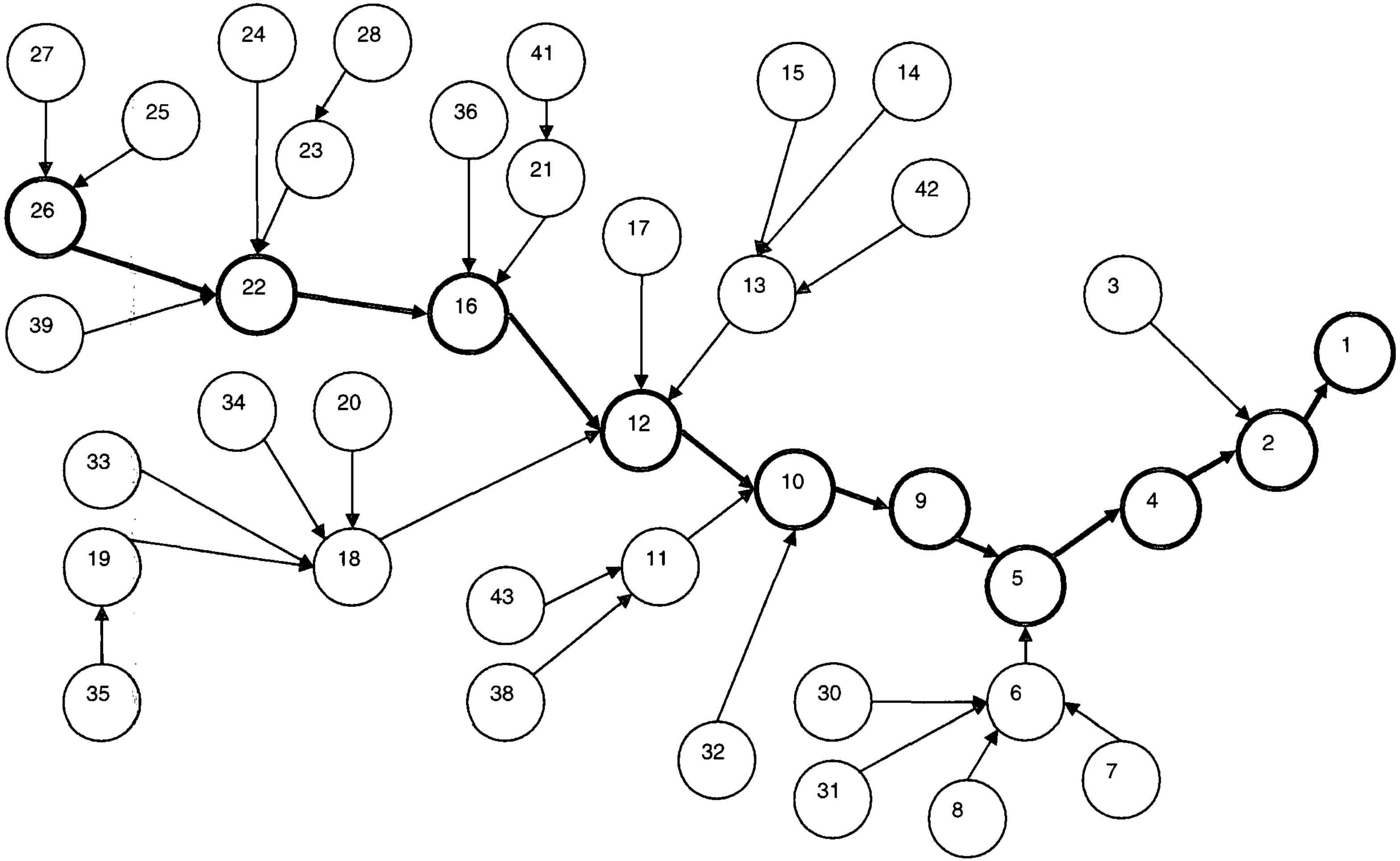


Figure 5.1 Schematic diagram of the sampling catchments. Numbers are those used throughout. Bold symbols indicate the main branch of the River Tees

Catchment id	*Catchment name*	*Outlet grid ref*
1	Tees at Blackwell Bridge (Broken Scar)	NZ 270125
2	Tees at Piercebridge	NZ 212156
3	Langley Beck at Gainford	NZ 156176
4	Tees at Winston	NZ 142163
5	Tees at Whorlton Lido	NZ 107146
6	Greta at Greta Bridge	NZ 087132
7	Gill Beck	NZ 062105
8	Eller Beck	NZ 031118
9	Tees at Eggleston Abbey	NZ 065150
10	Tees at Barnard Castle / Startforth	NZ 048162
11	Balder at Cotherstone	NZ 009200
12	Tees at Eggleston Hall	NY 997233
13	Eggleston Burn at B6282 road	NY 989240
14	Little Eggles Hope	NY 992290
15	Eggleston Burn at Middle End Farm	NY 985288
16	Tees at Middleton	NY 945253
17	Hudeshope Beck at Middleton	NY 946254
18	Lune at B6277 road	NY 960240
19	Lune Head Beck	NY 866206
20	Beck at Wemmergill Hall	NY 900219
21	Bowlees Beck	NY 907282
22	Tees below High Force	NY 889283
23	Langdon Beck at Intake Farm	NY 853310
24	Harwood Beck at Intake Farm	NY 859310
25	Widdybank site	NY 818304
26	Tees at Cauldron Snout	NY 814288
27	Crook Burn at B6277 road	NY 781358
28	Langdon Beck at Weardale road	NY 850330
30	Greta above Sleightholme confluence	NY 951121
31	Sleightholme Beck	NY 964111
32	Deepdale Beck	NY 991155

Catchment id	Catchment name	Outlet grid ref
33	Long Grain	NY 867208
34	Hargill Beck	NY 895217
35	Rennygill Sike	NY 863204
36	Etters Gill	NY 893285
38	Hunder Beck	NY 933181
39	Maize Beck	NY 812283
41	Flushiemere	NY 910302
42	Blackton Beck	NY 995250

Table 5.1 Numbering and location of catchments

Run number	Date of sampling	Number of samples analysed
1	04/06/2003	7
2	30/06/2003	22
3	19/11/2003	26
4	09/06/2004	22
5	07/12/2004	17
6	02/03/2005	17
7	28/09/2005	19

Table 5.2 Dates of sampling runs

5.2.2 Sampling and analysis protocol

Samples were collected and analysed from a total of 38 unique sites, in various combinations on each of seven sampling runs, as described in chapter 4. Dates of the sampling runs are given in Table 5.2. The samples used were the same as those used for the DOC analysis described in chapter 4 (subsamples were taken for each analysis). Sample collection bottles were acid washed and pre-rinsed with sample water. Samples were collected either via direct immersion of the bottle into the flowing water halfway up the water column, or using a weight-operated remote sampler held at a similar location in the stream.

Due to time constraints and also to the iterative nature of the DOC study, not all sites were sampled on each occasion. Furthermore not all the samples collected as described in chapter 4 were analysed in this study – some samples were lost due to equipment failure. The number of samples analysed from each day varied from 7 (the low figure is because several samples from this day were lost) to 26. Three precipitation samples were also collected and analysed. In all, 133 samples were analysed from the seven sampling runs and the precipitation collection.

Samples were analysed for concentrations of aluminium, calcium, iron, potassium, magnesium, sodium, and silicon all analysed using the ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy) method. Analysis was conducted on unfiltered samples using a Perkin Elmer Optima 3300 RL ICP-OES machine, and ICP Winlab was used for machine control and data processing. Mixed standards for analysis were produced using Romil ICP standards and a serial dilution technique; concentrations of elements in the standards are given in Table 5.3. Standards (including blanks) were run prior to the analysis, and the 50 and 25mg l^{-1} Ca standards were re-analysed as samples approximately every 25 samples as a manual check for drift; additionally all standards were re-analysed at the end of each run.

Two wavelengths were collected for each element except K, and all calibration curves used for data processing had R^2 values > 0.99 for all elements. Instrument drift was corrected during data post-processing using the internal standard method. Yttrium was selected for the internal standard as it was not found at detectable levels in any samples. All standards and samples were "spiked" with 1mg l^{-1} Y. Optical sensor output counts for each element are converted into mg l^{-1} concentrations by comparing counts for Y between samples and standards, so the Y spike must be accurately metered. Pipettes used were calibrated using a 5-place balance. Samples were acidified using 10mg l^{-1} HNO_3; this was found necessary to prevent flocculation of the samples on addition of the Y spike and subsequent clogging of the ICP sampling mechanism. Analysis was conducted on unfiltered samples which were stored frozen in sealed containers prior to analysis; samples were analysed immediately following addition of the HNO_3 and the Y spike.

Al	*Ca*	*Fe*	*K*	*Mg*	*Na*	*Si*
1	100	5	5	5	10	5
0.5	50	2.5	2.5	2.5	5	2.5
0.25	25	1.25	1.25	1.25	2.5	1.25
0.125	12.5	0.625	0.625	0.625	1.25	0.625

Table 5.3 ICP standard concentrations

5.3 Preliminary Results

5.3.1 Analysis of solute concentrations

Box-whisker plots of the concentration range for each element in each sampling run are shown in Figure 5.2. The upper and lower box boundaries mark the 75th and 25th percentiles respectively and the centre line represents the median. Interquartile range (IQR) is defined as the difference between the 75th and 25th percentiles. Whiskers extend to the most extreme values which fall within the upper and lower adjacent ranges, which are defined as (75th percentile + 1.5*IQR) and (25th percentile – 1.5* IQR) respectively. Clearly the solutes show a wide range of concentrations, and there are few outliers. The concentrations of each solute vary differently between the sampling runs, with the exception of the first two sampling runs where concentrations are generally low (note that only 7 samples were analysed from the first run).

Two key anomalies stand out: much higher Ca^{2+} concentrations in the fourth sampling run compared to other dates, and much higher Na^{+} concentrations in the sixth run. The individual Ca^{2+} concentrations for each sample in the fourth run are shown in Figure 5.3. The high concentrations are found in a wide range of catchments and no clear geographical pattern can be discerned: high concentrations are observed in both large and small catchments (e.g. Greta vs. Widdybank) and both northerly and southerly catchments (e.g. Hudeshoe Beck vs. Greta). The river Tees was sampled at four locations on the fourth run (Cauldron Snout, Middleton, Eggleston Hall, Broken Scar) and the concentration of Ca^{2+} increased downstream along the river (Figure 5.3). There is some evidence to suggest that the concentration is lower in catchments with higher peat cover (e.g. Cauldron Snout, Little Eggles Hope) but this is clearly not a consistent pattern (e.g. the high value for the entirely peat-covered Widdybank catchment) because catchments may be high in peat cover in addition to containing water / rock interactions. Antecedent weather conditions were extremely dry for this run and all samples were taken at very low flow. The higher calcium concentrations are likely to reflect either a higher relative contribution from a Ca^{2+}-rich groundwater, or from water contact with outcrops within the catchment, normally diluted by higher flows. In chapter 4, no good relationships could be found between DOC concentration in samples from the fourth run and catchment characteristics and this was suggested to be due to the samples on this day not containing much surface water; these data lend weight to that suggestion.

The high Na^+ values in the sixth sampling run are harder to explain in terms of natural variations in flow pathways. Na^+ is commonly taken as an indicator of (oceanic) rainwater contribution and this sampling run took place during the early stages of a snowmelt episode, so it would not be surprising to find samples in this run closely related to precipitation. However, the second sampling run also took place under rainy conditions and there is no evidence of increased Na^+ concentrations in these samples. Whilst the concentration of Na^+ in precipitation does vary greatly dependent on atmospheric circulation (unfortunately precipitation samples were not available for either of these dates) it seems unlikely in any case that this would be sufficient to raise the concentrations to the extent observed. A more plausible explanation would be the contribution of road salt: roads were observed to be heavily salted due to the cold weather in the days prior to this sampling run. Figure 5.4 shows the individual Na^+ sample concentrations for this run: this largely confirms the road-salt hypothesis. The Greta above the Sleightholme confluence runs parallel to and downslope of the A66 trunk road, and would receive drainage water from this road. Similarly the Langdon Beck at Intake Farm will receive drainage water both from the (regularly salted) Langdon Beck – St John's Chapel road and the B6277. Slightly surprising under this hypothesis is the low Na^+ concentration in the Lune, as the road running up this catchment is also regularly treated; however, Selset and Grassholme reservoirs are close above the sampling point and would buffer the Na^+ spike. Lunehead Beck and Long Grain are parallel streams with similar catchments (and snow cover at the time); however, the B6276 drains into the former and subsequently this exhibits a higher Na^+ concentration as expected.

It could therefore be argued that some of the data should be excluded from the analysis. Certainly the likely Na^+ contamination by road salt in the sixth sampling run means that the scores for these samples should not be interpreted in terms of precipitation influence on Na^+ and its associated components in a PCA, and perhaps also that the Na^+ data from this run should not be included in the PCA analysis in the first place. Rather than skew the analysis by selectively excluding only "contaminated" samples, all data from this run were excluded from the PCA. As to the Ca^{2+} increase in the fourth run – there is nothing to suggest that these data should be excluded, as they merely represent a different set of flow pathways and water sources

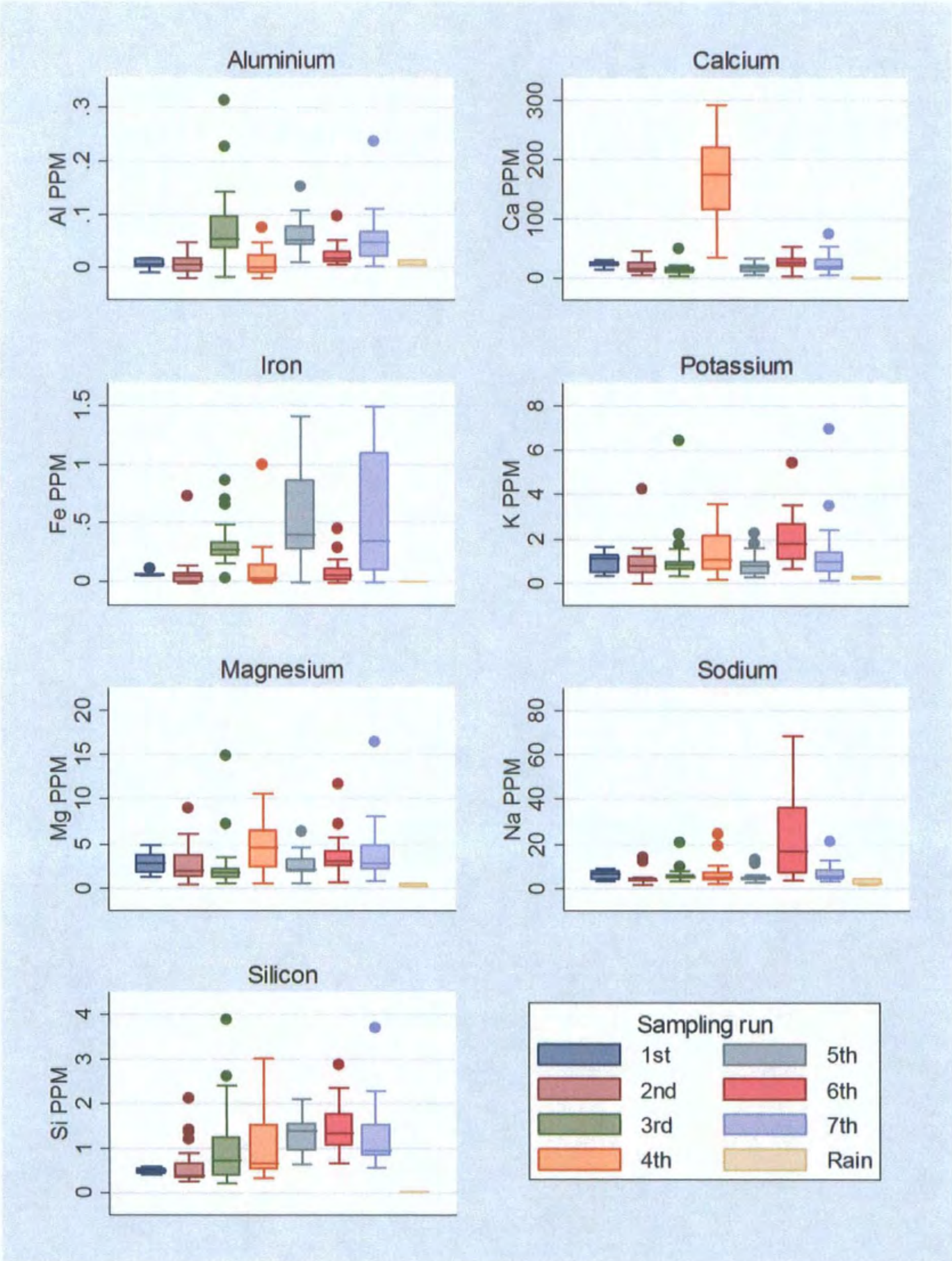


Figure 5.2 Box-whisker plots of solute concentrations by run. See figure 4.22 for DOC concentration data.

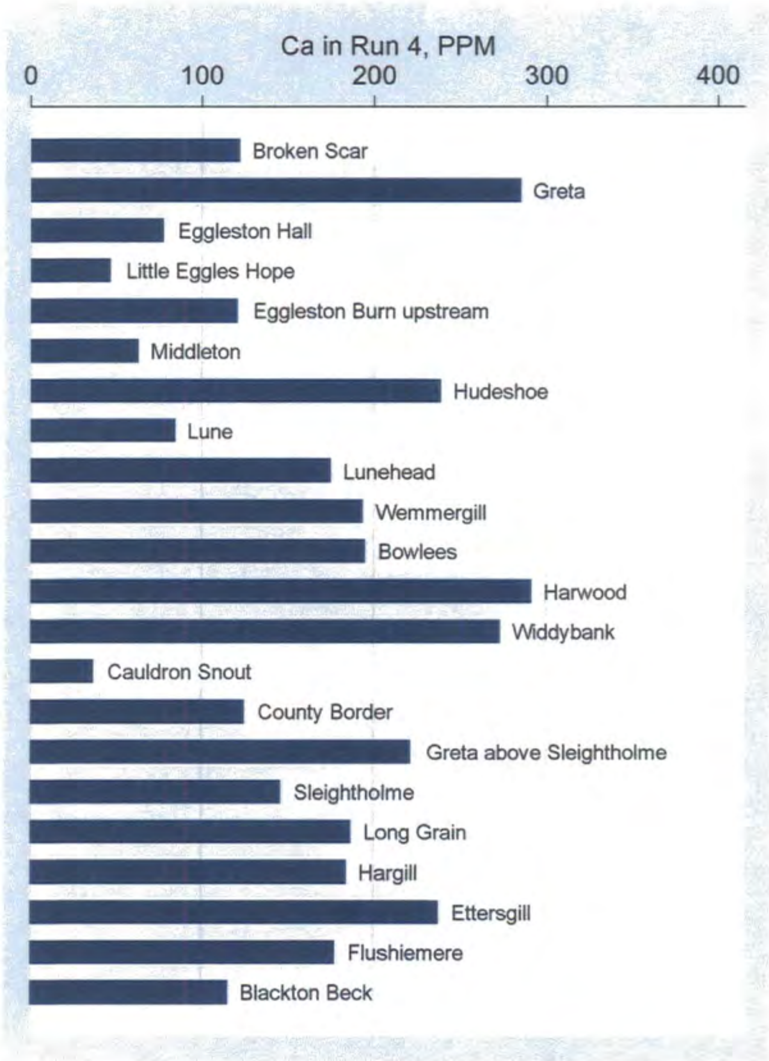


Figure 5.3 Calcium concentrations in the fourth sampling run

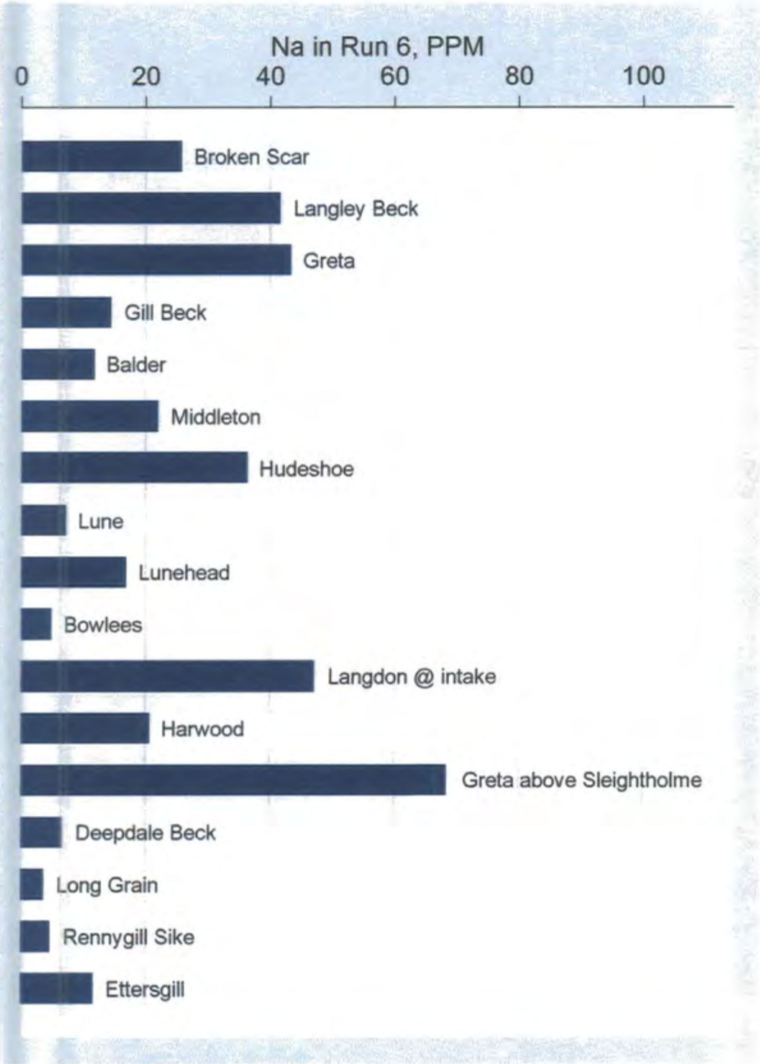


Figure 5.4 Sodium concentrations in the sixth sampling run

5.4 PCA results

5.4.1 Analysis output

Most solute concentrations were significantly correlated (p > 0.95), but correlation coefficients are not particularly high (Table 5.4). Therefore the variables were judged to be sufficiently independent that all should be used in the PCA; no variables were eliminated. A principal components analysis was run on these 8 variables (Aluminium, calcium, iron, potassium, magnesium, sodium, silicon and DOC) for data from all the sampling runs except the 6th, and including the precipitation samples. Although all variables in this study are on the same scale (mg l^{-1}) the range of values is large and so the analysis was run using the correlation matrix. The number of components to retain was based on including all those with an eigenvalue > 1 plus the first component with an eigenvalue < 1 (Table 5.5). The scree test was also applied, graphing the eigenvalues against the number of components and identifying the number of components at which a break in slope occurred (Figure 5.5). Both methods had the same results, indicating the retention of 3 components. The variable loadings of each of these three components are compared in Figure 5.6 – Figure 5.8.

	Al	*Ca*	*Fe*	*K*	*Mg*	*Na*	*Si*	*DOC*
Al	1							
Ca	-0.3944	1						
Fe	0.6323	-0.2935	1					
K	-0.2743	0.2998	-0.2201	1				
Mg	-0.3704	0.4667	-0.2689	0.9053	1			
Na	-0.1391	0.2865	0.0166	0.7134	0.6706	1		
Si	-0.0958	0.1024	0.0839	0.6061	0.6676	0.4753	1	
DOC	0.7482	-0.4024	0.8373	-0.324	-0.4184	-0.104	-0.0915	1

Table 5.4 Correlations of variables used in the PCA (data from run 6 excluded). Shaded cells indicate correlation significant with P<0.05

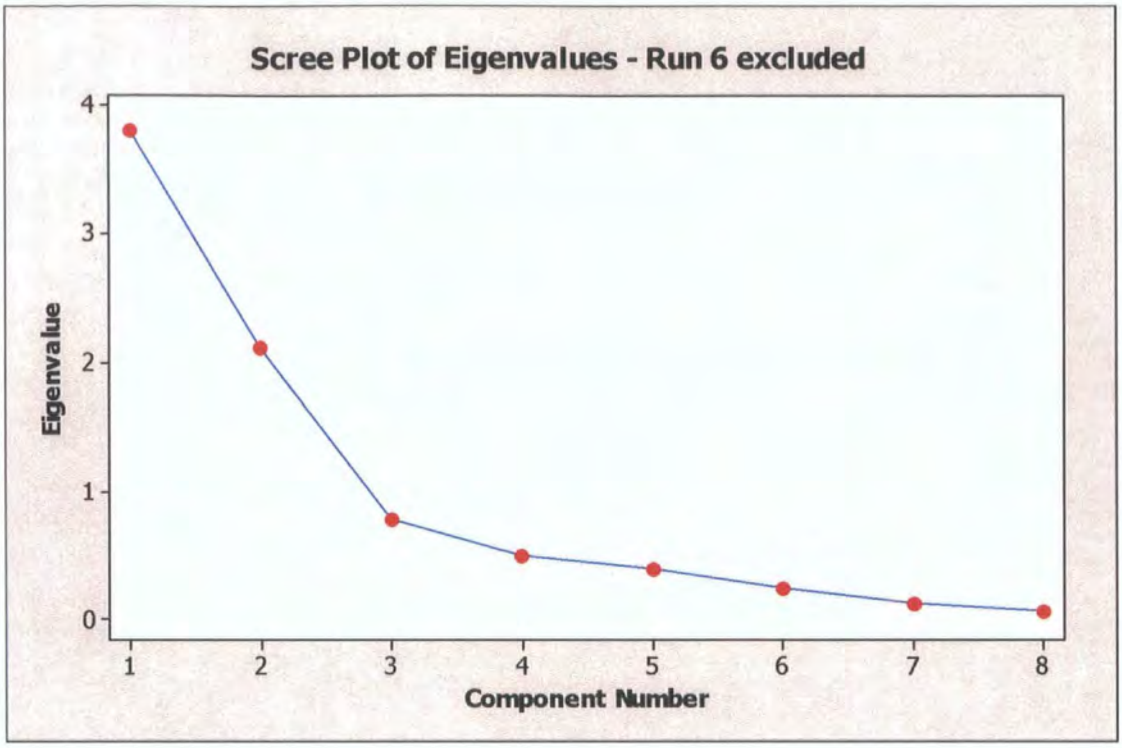


Figure 5.5 Eigenvalues from PCA on 8 variables

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
Al	0.331	0.384	-0.087	-0.155	-0.764	0.301	-0.194	-0.004
Ca	-0.300	-0.100	-0.859	0.329	-0.148	0.068	0.105	-0.128
Fe	0.279	0.496	-0.214	0.233	0.396	-0.256	-0.588	-0.087
K	-0.431	0.269	0.118	-0.248	-0.217	-0.498	0.042	-0.608
Mg	-0.464	0.223	0.028	0.032	-0.199	-0.331	-0.132	0.753
Na	-0.334	0.360	-0.173	-0.571	0.373	0.512	0.004	0.043
Si	-0.289	0.389	0.375	0.652	0.009	0.394	0.167	-0.130
DOC	0.356	0.439	-0.155	-0.026	0.108	-0.254	0.747	0.144
Eigenvalue	3.798	2.115	0.773	0.499	0.392	0.237	0.126	0.060
Proportion variance explained	0.475	0.264	0.097	0.062	0.049	0.030	0.016	0.007
Cumulative variance explained	0.475	0.739	0.836	0.898	0.947	0.977	0.993	1.000

Table 5.5 All 8 components from the initial PCA. Components 1-3 were retained.

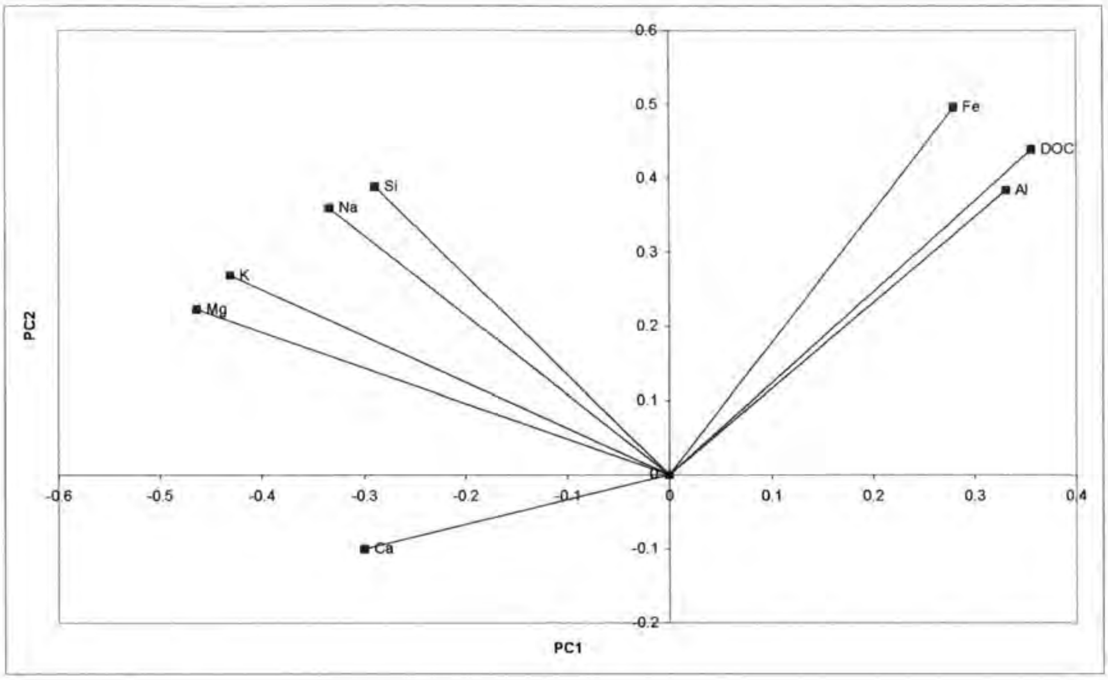


Figure 5.6 Loading plot of PC1 vs. PC2

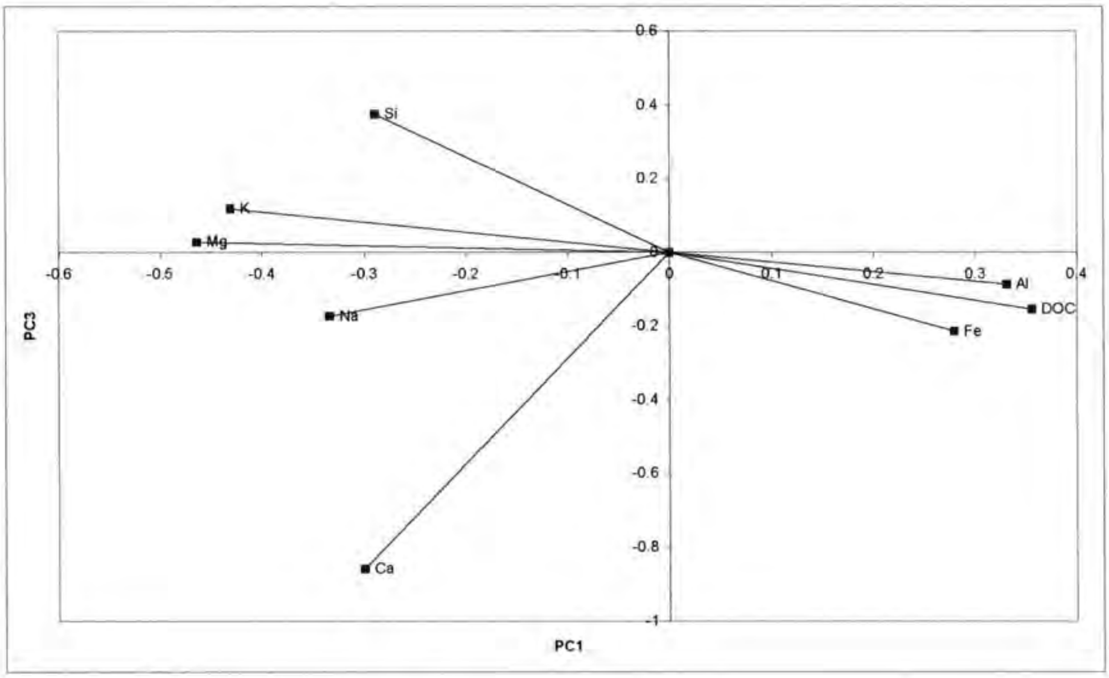


Figure 5.7 Loading plot of PC1 vs. PC3

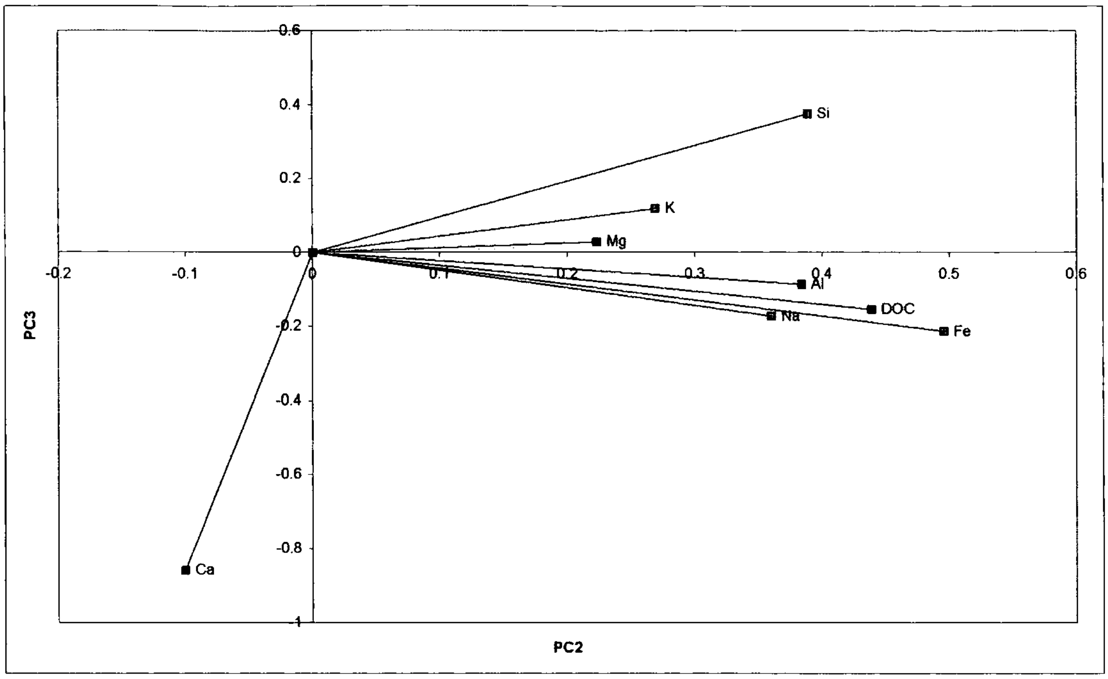


Figure 5.8 Loading plot of PC2 vs. PC3

Component 1 is often found to represent an overall concentration or size, with similar loadings on most variables (e.g. Worrall et al, 2003b; Manly, 1986). However this appears not to be the case in this analysis with PC1 having opposite sign on Al, Fe and DOC compared with the other 5 variables. Instead this component is likely to represent the influence of peat surface waters, with Al and Fe often being associated with such waters along with DOC. (It should be noted that it is the relative sign of the loadings between variables that is important, e.g. in PC1 above Al and Ca take opposite signs; the signs of an entire component can be reversed without this having any bearing on the underlying relationship, as a consequence of the matrix manipulation in the PCA procedure (Section 3.4.1)). K and Mg have large loadings of opposite sign to Al, Fe and DOC, and this could indicate that the component contrasts peat surface waters with precipitation-derived water, especially continentally-derived precipitation. Component 1 can therefore be seen as contrasting peat-derived surface waters with all other waters.

Component 2 seems more likely in this analysis to be the component linked to overall concentration, with medium loadings of identical sign on all variables except Ca – this exception is not necessarily too surprising due to the high concentrations of Ca in the samples from run 4, which could mask the overall Ca loading in this general concentration component. Component 3 is dominated by a very large loading on calcium, together with a substantial loading of opposite sign on silicon. This is likely to represent a groundwater influence in the samples, given the limestone geology of the area, which is particularly observed in Run 4 but not exclusively so (e.g. Figure 5.14). Component 3 therefore chiefly identifies samples from run 4 in these data, due to the much higher Ca concentrations in this run.

5.4.2 Component scores and trends

The first three PCs were scored for the entire dataset and are plotted against one another in Figure 5.9. The overall distribution of these plots suggests at least two trends: firstly, increasing PC1 against increasing PC2, and secondly increasing PC1 against decreasing PC2. PC3 shows less clear trends against the other two components; there is evidence of an increasing PC3/decreasing PC2 vs. increasing PC3 / increasing PC2 distribution, but not all the samples fall within this trend (Figure 5.9).

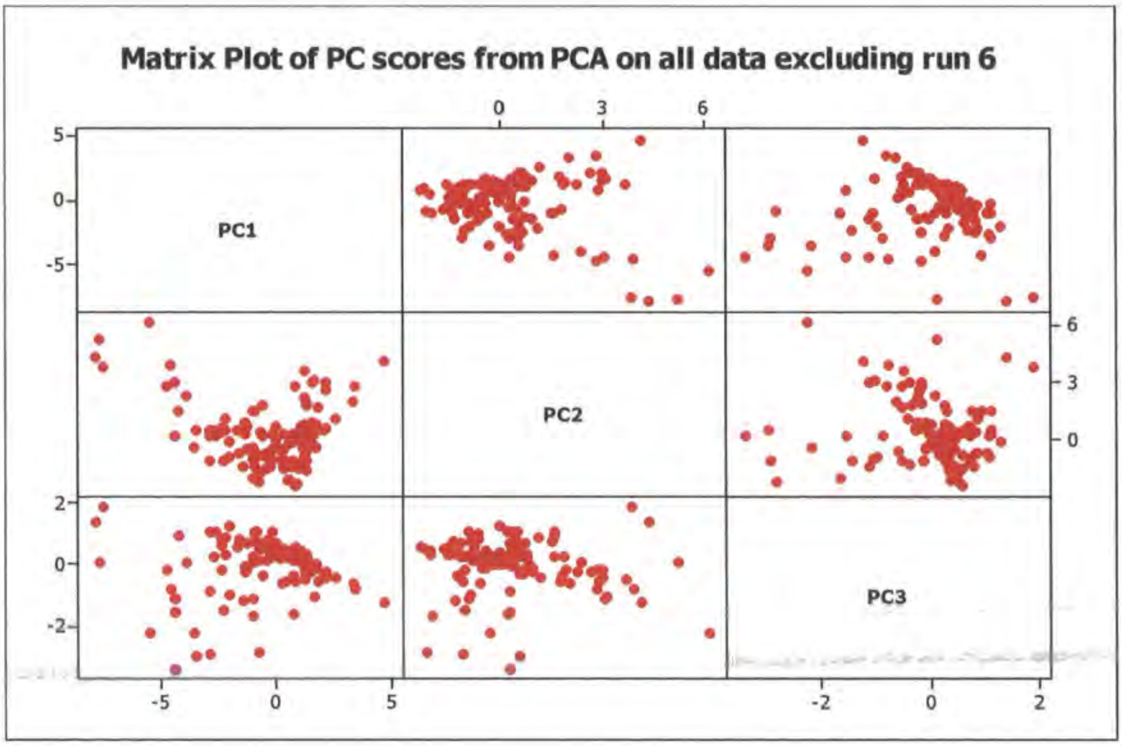


Figure 5.9 Overview of scores from the first three PCs

Figure 5.10 shows PC1 plotted against PC2, grouped by sampling site. In the relationship between the components three end members appear to be present: Langley Beck, Rennygill Sike, and rainwater. This plot helps to confirm the interpretation given to PC1 above, with the end members relative to this component being Langley Beck (a lowland, peat-free catchment) and Rennygill Sike, an upland peat first-order stream, predicted and observed in chapter 4 to have high DOC export concentrations. Precipitation samples have loadings close to zero on PC1, confirming that PC1 represents two different evolutionary trends from the input rainwater, one towards positive PC1 and one towards negative PC1. As to PC2, rainwater samples represent an end member of low PC2 scores, contrasting with both low-order peatland samples (e.g. Rennygill) and lowland streams (e.g. Langley Beck) which both have high positive PC2 scores, confirming the nature of PC2 as an overall concentration component (Figure 5.10). Displaying the loadings of PC1 and PC2 against one another (Figure 5.6) aids the interpretation of these scores illustrating that the trend from rain towards peat-sourced samples (increasing positive PC1 and PC2, e.g. Rennygill Sike) is one of increase in Fe, Al, and DOC, whilst increased PC2 represents increased concentration in all solutes except Ca.

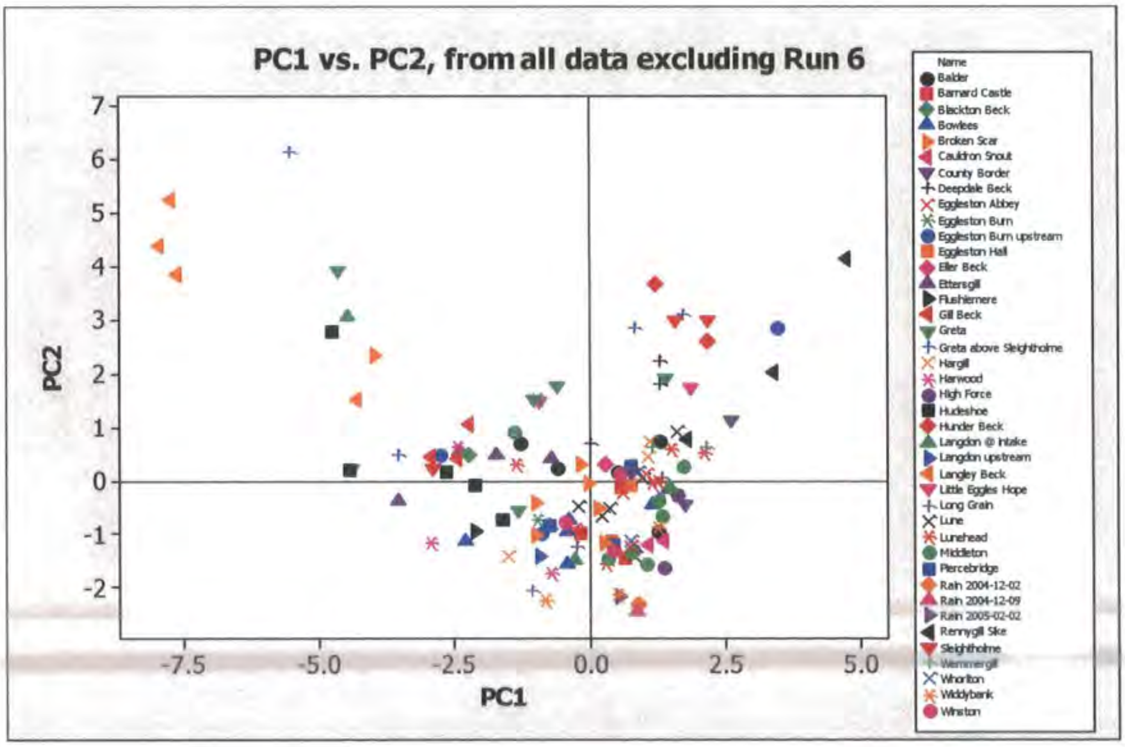


Figure 5.10 PC1 against PC2 grouped by sampling site

Figure 5.11 shows PC1 against PC3 grouped by sampling site. The same two end members (Langley Beck and Rennygill Sike) can be observed on PC1 as previously, but patterns are much less well defined on PC3. There is a strong trend from high negative PC1 / high positive PC3 to high positive PC1 / high negative PC3, but there is considerable scatter on PC3 which appears to apply across a wide range of the sampling sites and obscures the trend – many samples fall below this trend on PC3. A similar problem is observed with the plot of PC2 against PC3 (Figure 5.12) – here there is a well defined trend among samples with higher PC2 scores, but samples with low negative PC2 scores are more scattered across PC3. (Figure 5.12) Examination of the relevant loading plots (Figure 5.7 and Figure 5.8) suggests that the scatter in both cases is due to high Ca concentrations.

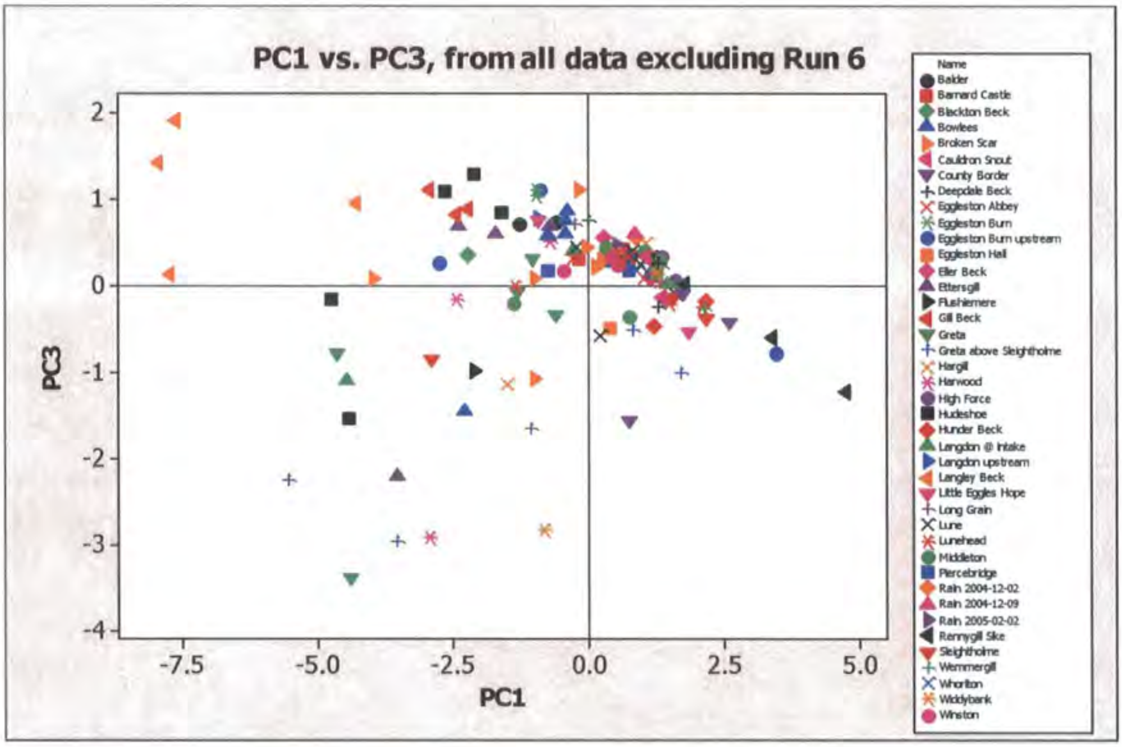


Figure 5.11 PC1 against PC3 grouped by sampling site

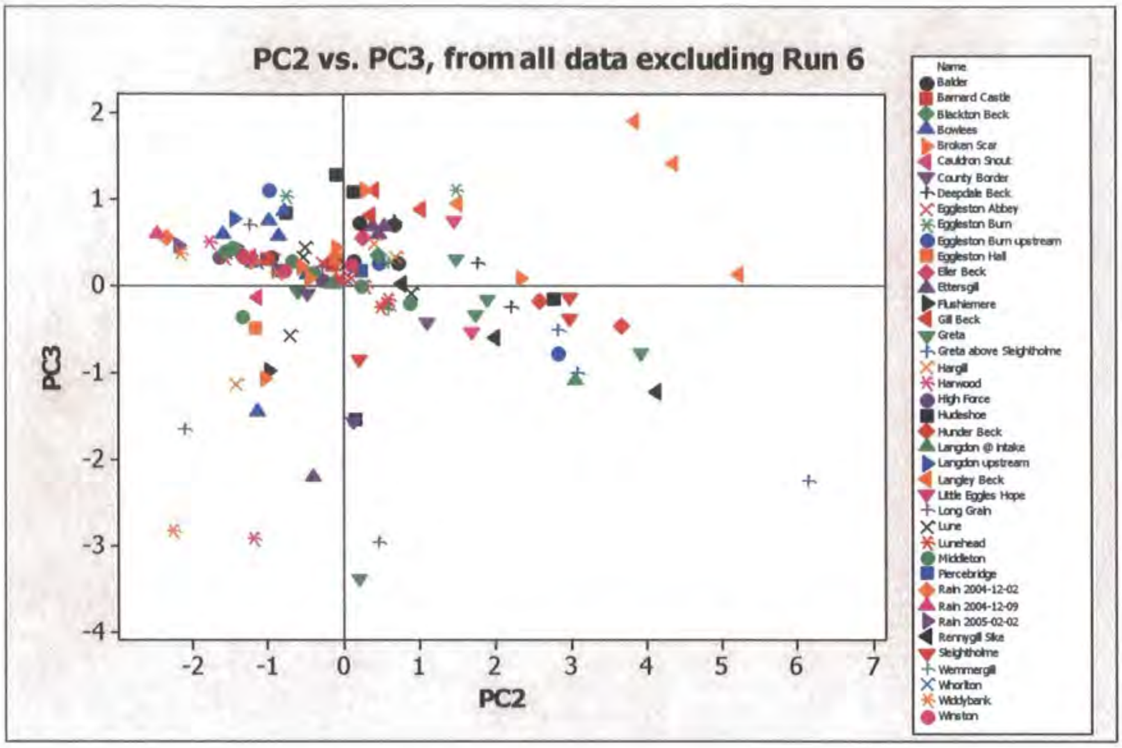


Figure 5.12 PC2 against PC3 grouped by sampling site

If the data are displayed grouped by sampling run (Figure 5.13, Figure 5.14, Figure 5.15), then considerable clustering according to sampling run can be observed, and in particular the variation across PC3 becomes clearer. In the plot of PC1 against PC2 the samples do, to some extent, group by sampling day, with for instance samples from run 3 having more positive PC1 scores, and the samples from run 2 having lower absolute scores on both PC1 and PC2 (Figure 5.13). However despite this most of the trends and the relationship between PC1 and PC2 can be observed independently of sampling run, in that the end members suggested previously are observed in more than one sample run: the Langley Beck end member is represented in runs 3, 6 and 7 and the Rennygill Sike end member is represented in runs 5 and 7. Furthermore, the remaining samples from each of these sites lie along the same trends if in a less extreme position.

By contrast in the PC1 / PC3 and PC2 / PC3 plots it can be identified that samples from run 4 have far more negative scores on PC3 than those from any other run. This is not surprising in context of the identification of PC3 as being influenced primarily by Ca (Figure 5.7 and Figure 5.8), and the observed baseflow conditions prevailing when samples from Run 4 were collected. With reference to PC2 / PC3, the sampling runs can all be said to be similar with the exception of run 4; trends will be analysed discounting samples from this run.

Similarly for PC1 / PC3, samples from run 6 also plot lower on the PC3 axis than the main trend from the other 5 runs. This can be explained by the high observed Na concentrations in run 6 discussed earlier.

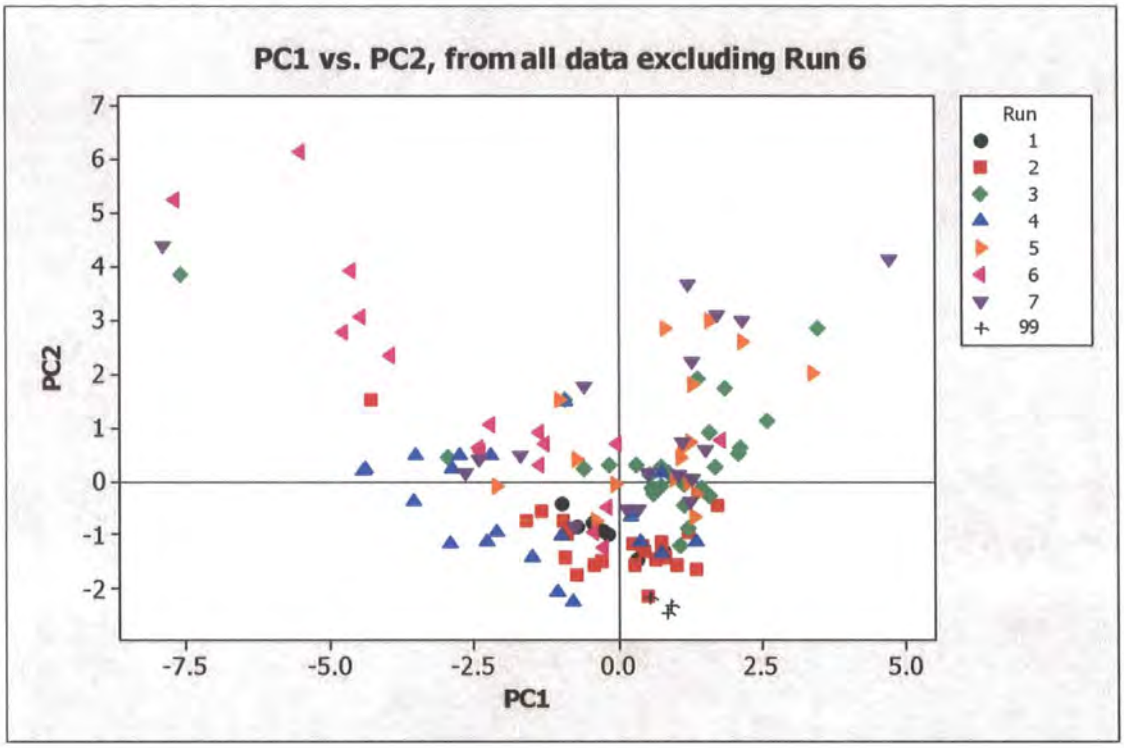


Figure 5.13 PC1 against PC2 grouped by sampling run

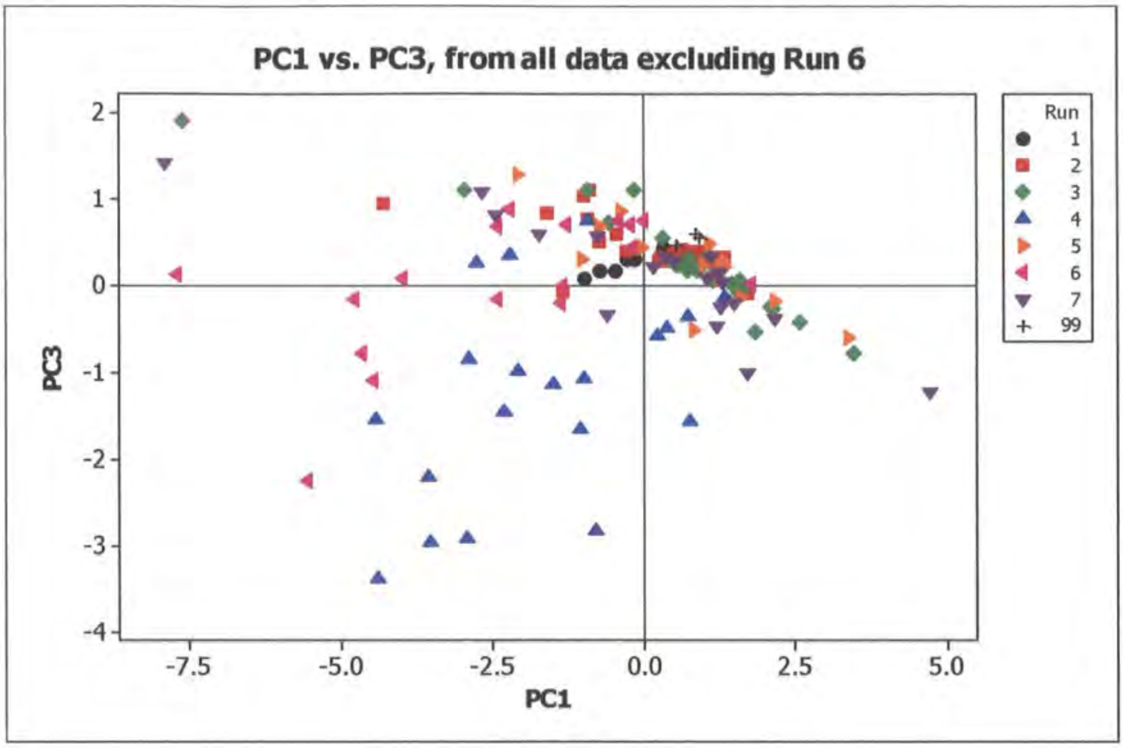


Figure 5.14 PC1 against PC3 grouped by sampling run

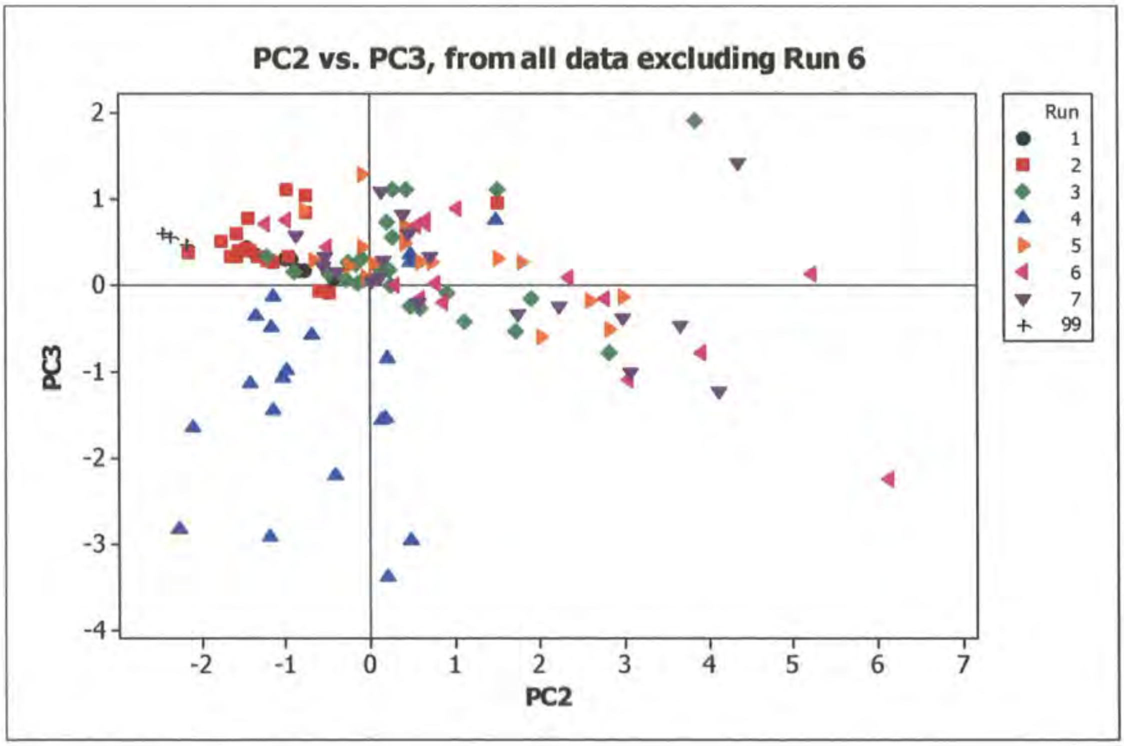


Figure 5.15 PC2 against PC3 grouped by sampling run

5.5 Spatial distribution of component scores relative to catchment nesting

With the caveats regarding systematic differences between sampling days described in section 5.4.2, the distribution of samples on the PC score plots can be assessed relative to the catchment schematic in Figure 5.1. The most deeply-nested series of catchments sampled was the main branch of the River Tees; this was sampled variously at several locations as summarised in Table 5.6. Because these catchments are nested, the development of the water as it moves down the catchment can be described.

ID Number	*Site Name*	*Runs sampled*	*River length above sampling point (km)*
1	Broken Scar	1,2,3,4,5,6,7	81.6
2	Piercebridge	1,2,3	73.5
4	Winston	1,2,3	65.3
5	Whorlton	2,3	60.5
9	Eggleston Abbey	1,2,3,7	55.7
10	Barnard Castle	1,2,3	53.6
12	Eggleston Hall	3,4	42.6
16	Middleton	1,2,3,4,5,6,7	35.8
22	High Force	1,2,3	28.7
26	Cauldron Snout	3,4	17.7

Table 5.6 Summary of sampling sites on main River Tees branch

Sampling run	*Number of river samples*
1	7
2	8
3	10
4	4
5	2
6	2
7	3

Table 5.7 Number of samples taken from River Tees by sampling day

For those sample runs where the river was sampled enough times for a trend to be identified (i.e. three or more times, Table 5.7) relationships can be identified between the principal component scores and the position in the river network (measured by the river length to sampling point).

5.5.1 PC1

For PC1, scores in general decrease down the river (Figure 5.16). The relationship was significant ($P < 0.01$) for all sampling runs except run 7 (where there were only 3 river samples). This can be interpreted as a decreasing peat-source character or increasing groundwater character along the river length. The relative scores on PC1 for each site, in addition to the gradient of the trend, vary by run and there is some evidence to suggest that this is related to flow characteristics: sample runs 1 and 4 took place under baseflow, whilst runs 2 and 3 took place after or during rain (section 4.8.3) (as did run 7; however, with only three data points this trend is less well defined). The trends for the baseflow runs are very similar to one another as are those for the quickflow runs. Furthermore the trends for the quickflow samples exhibit considerably more scatter than those for the baseflow samples.

Precipitation samples ranged between 0.56 – 0.92 on PC1 (Figure 5.10), and relative to PC1 there is a point along the river where the water has a composition, relative to PC1, that is identical to rainwater – that is, where the influence of the two old water types (peat-influenced vs. rock-influenced) identified in section 5.4.1 is in equilibrium. This occurs at some point between High Force and Barnard Castle during baseflow, and not until the lower reaches of the catchment if at all during quickflow. This implies that during quickflow the influence of peat surface waters (high PC1 scores) on the composition of the river water is relatively greater; the effect of precipitation is to increase near-surface flow from peat areas. An increase in near-surface flow in general is as would be expected in a catchment with a "flashy" hydrograph regime such as this one; however since PC1 distinguishes primarily between peat surface waters and all other waters, this trend should be distinguished from a surface water / groundwater contrast. Both of these sampling runs (2 and 3) were characterised by quickflow conditions throughout the catchment including subcatchments with low PC1 scores (e.g. Langley Beck) as well as those with high PC1 scores; there was rain throughout the day for run 2, and rain on the preceding day for run 3 (personal observations: no distributed rainfall or flow data were available). However since the overall observed effect is higher scores on PC1 in the Tees on these wet days, it would appear that rainfall increases near-surface runoff from the peat catchments to a greater extent than it does from catchments such as Langley Beck.

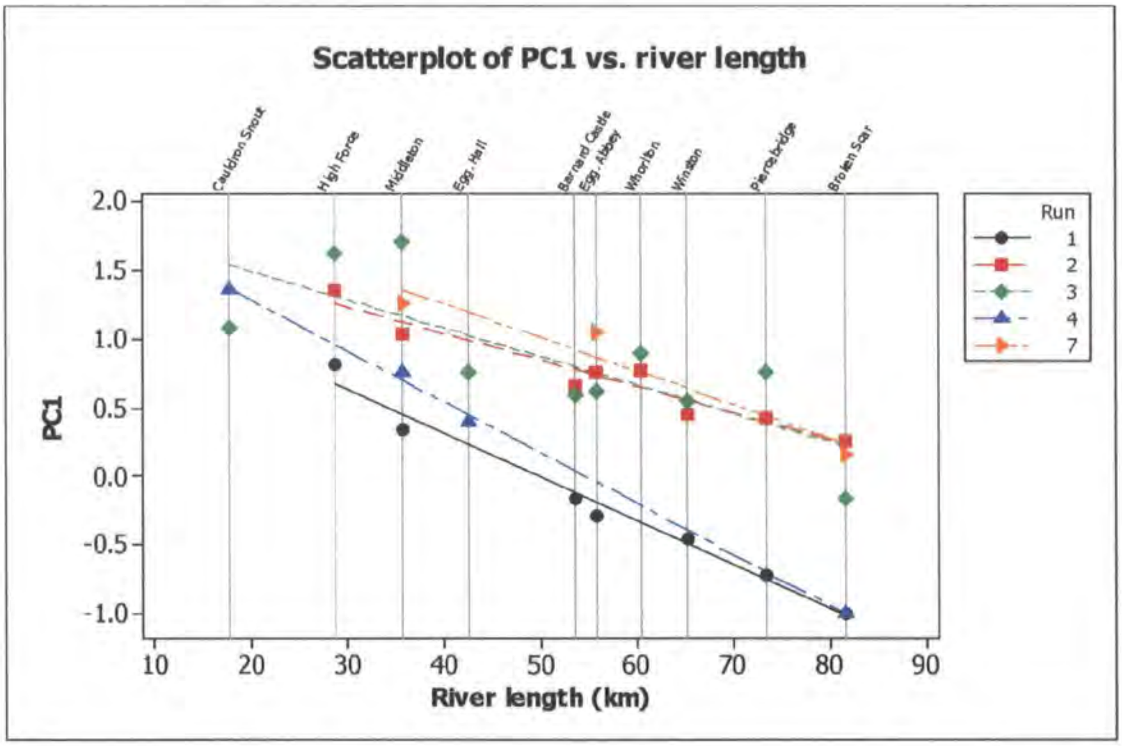


Figure 5.16 Scatterplot showing the relationship of PC1 to position on the main river channel

5.5.2 PC2

Assessing PC2 in the same way (Figure 5.17) is not as informative. Significant trends exist between river length and PC2 for sampling runs 1, 2 and 3; however, no significant relationship exists for run 4. The general trend is an increasing PC2 score (increasing overall concentration) downstream. Samples taken in run 3 have substantially higher scores than the other runs, suggesting the river chemistry was more concentrated on this day; however sample runs 2 and 3 were both taken under quickflow conditions and equivalent high PC2 scores are not observed for run 2. One possible explanation for this difference between runs 2 and 3 is that run 2 took place after a lengthy dry period and during actual rainfall. These samples may therefore be represented by a higher proportion of infiltration-excess overland flow or macropore flow following dessication, leading to the samples having relatively little interaction either with soils or bedrock and remaining little-altered from precipitation. Conversely run 3 took place when flows were high but nonetheless after (rather than during the early stages of) a reasonable period of rain, which could plausibly mean soils had become more thoroughly wetted, decreasing infiltration-excess overland flow, in which case more runoff from both soils and groundwater would contribute to the river water, increasing overall concentration.

If the low flows and antecedent dry conditions of sampling run 4 are taken to indicate that samples on this day were derived from a higher proportion of groundwater than other days, then the generally low PC2 scores for run 4 together with the lack of downstream trend suggest two important observations. Firstly, that groundwater contributes to the river flow throughout the whole catchment, including in the peat-covered upper reaches. If groundwater did not contribute significantly to the shallow peatland upper catchments, then PC2, representing general concentration, would be expected to increase downstream in the absence of any diluting influence. If on the other hand, groundwater contributes throughout the catchments, then PC2 scores would be expected not to increase along the river system – as is observed (Figure 5.17, Figure 5.10). However, this is not a safe conclusion as will be shown in the discussion of PC3 below.

Secondly, sites such as Langley Beck cannot simply be explained as representing a baseflow contrasting with the largely quickflow water from peatland catchments such as Rennygill Sike. Langley Beck samples have high positive scores on PC2 whereas samples from run 4 (throughout the entire system, not just the River Tees: Figure 5.13) have low scores on PC2, and therefore the high positive scores for Langley Beck cannot be explained purely as a groundwater influence – the low PC2 scores in run 4 suggest that groundwater-derived baseflow is not likely to contribute a sufficiently strong influence or concentration to account for the high PC2 scores observed at Langley Beck. (Unfortunately Langley Beck was not sampled on run 4). Some other process is required to account for the high PC2 scores (high concentration) in Langley Beck, such as in-stream contact with silicon or magnesium rich rock or clay, or a different aquifer source to that sustaining baseflow throughout the catchment.

This observation regarding Langley Beck, referring back to the interpretation of PC1 as a contrast between Rennygill Sike and Langley Beck, implies that PC1 represents a contrast between peat water and another water (which may be a different surface runoff, or a groundwater source) which sustains baseflow and which was largely sampled in run 4, and is different again from the source rainwater.

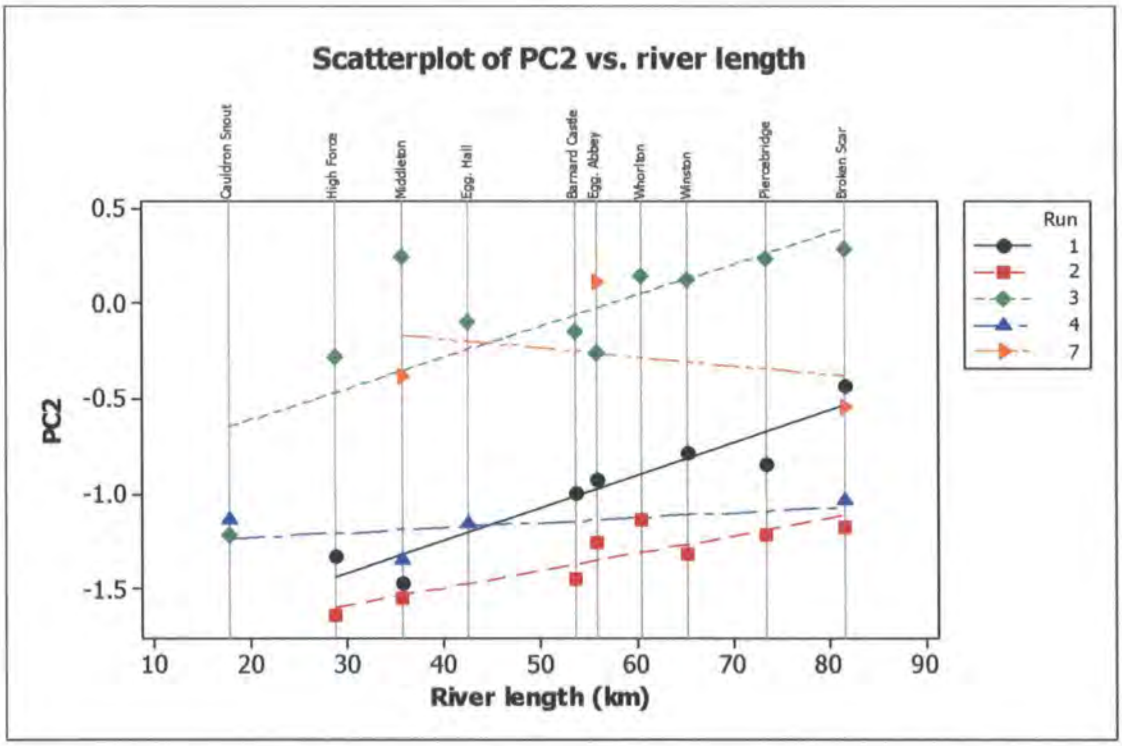


Figure 5.17 Scatterplot showing the relationship of PC2 to position on the main river channel

5.5.3 PC3

Comparing PC3 with the river length (Figure 5.18) shows a significant relationship ($p < 0.05$) only for runs 1 and 4; the trend for run 1 whilst significant is extremely shallow and so only that for run 4 is assessed here. According to the interpretations above the decreasing trend in PC3 downstream represents an increasing groundwater influence, or more specifically from the PC loadings (Figure 5.6 – Figure 5.8) an increasing Ca concentration. Scores across the catchment for PC3 are not so widely spread as for the other two components, with the exception of Run 4 which was clearly separated from the other sampling days for all sites on PC3 (Figure 5.11, Figure 5.12).

This trend could therefore represent the effect of increasing bedrock contact down the river, which has two possible explanations. Firstly, this may be due to a higher proportion of total flow being groundwater or in any case having greater contact with a calcium-rich source. Secondly the trend may be caused simply by the longer contact with limestone and other calcium sources downstream within the river channel that would be expected in a uniform catchment. The four river samples score in the mid range of PC3 scores from this run, with 10 other samples scoring lower on PC3 than the lowest-scoring river sample (Broken Scar) (Figure 5.12 and Figure 5.15). This suggests that the first explanation is correct: the decreasing PC3 trend down the river does represent an increased proportion of flow being in contact with a calcium-rich source. If only a longer contact time were responsible then the samples with the longest contact time of all (i.e. Broken Scar) would be expected to show the lowest score on PC3. In either case it would be reasonable to expect this trend to be swamped under high flow conditions, explaining the lack of observed trend in runs 2 and 3 (Figure 5.18).

However, explaining the run 4 trend in PC3 as an increasing groundwater influence does contradict the inference made from PC2 above that there is a groundwater influence throughout the catchment. With groundwater influence increasing down the catchment, why under conditions of minimal flow from surface waters (run 4) do PC2 scores not increase downstream (representing increased concentration)? One possibility is due to the fact that PC2 has an opposite loading on Ca to all the other variables. Since run 4 was generally high in calcium but low in overall concentration, this could confound the interpretation of PC2 trends for run 4. Another possibility is simply that PC2 did in fact increase downriver during run 4, but the scatter is too great in the 4 observed samples for this trend to be apparent. In either case, the hypothesis based on PC2 that there is a substantial groundwater influence throughout the catchment cannot be held confidently. It seems most likely, therefore, that PC2 represents a runoff from surface waters other than peat, whilst PC3 is the component representing baseflow and groundwater.

The only variable with a substantial positive loading on PC3 is Si (Figure 5.7). One likely source of this within the catchment is the clay till or gley soil layers beneath the peat. Such a source would also explain the (small) positive loading for potassium seen in this component. Worrall et al (2003b) found evidence of K in peat soil water that was explained as an influence of underlying high-CEC clays. This implies that the higher upstream values observed for PC3 in sample run 4 may also, or alternatively, point to seepage from these layers contributing to the observed runoff. This would concur with the results of Mulder et al (1995) who studied the small peatland Ingabekken catchment in Norway and concluded that the baseflow in this catchment was dominated by flow from the mineral soils beneath the peat. Branfireun and Roulet (1998) also found evidence of groundwater contributions to baseflow in a peat catchment, despite the common assumption that due to low hydraulic conductivity in the catotelm there is minimal water exchange between deep peat and the mineral layers beneath. Moving down the Tees catchment the proportion of peat cover decreases, in line with the observed trend in decreasing PC3. Alternatively, as silica has been found to mix non-conservatively and occasionally precipitate out of solution in the presence of SiO2 particles (Casey and Neal, 1986; Christophersen et al, 1990), a decreasing silica concentration downstream would not be unexpected. This suggests that the downstream trend in PC3 can be partially explained by aging of the water and consequent silica precipitation, but this would not account for the changes in PC3 due to Ca which would be expected to be larger given the relative PC3 loadings of Ca and Si. Nonetheless these options are not contradictory.

All these explanations for PC3 seem equally valid and do not contradict, and therefore high PC3 scores could be seen as representing the baseflow from peat catchments, possibly in addition to a smaller loading on water aging, with PC3 overall representing a contrast between the baseflow from peatland streams and from bedrock / rock outcrop –influenced streams. Trends in PC3 are far weaker in the other sampling runs due to the much larger percentage of flow coming from surface water (uninfluenced by either of these sources) and with reference to the Si / precipitation explanation, shorter residence times, at other times.

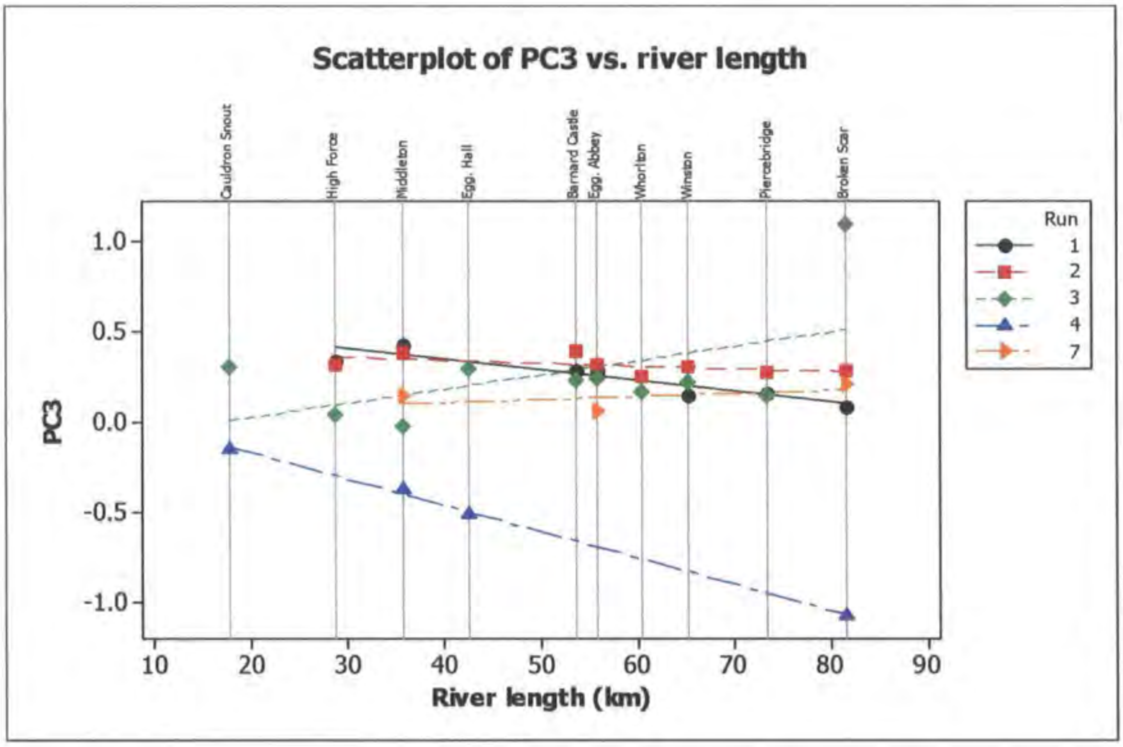


Figure 5.18 Scatterplot showing the relationship of PC3 to position on the main river channel

5.6 Source identification through PCA-based end member mixing analysis

The previous section has illustrated the use of the results of a Principal Components Analysis in conjunction with spatial details of the sampling sites to assess trends and infer their causes. Given a series of nested catchments, the development of trends in the sample chemistry downstream was illustrated and the likely causes behind these trends were used to infer the implied water sources, in terms of shallow / deep water, and peat / non-peat source areas. This was achieved from direct analysis of PC trends relative to sampling locations. Alternatively, as demonstrated by Worrall et al (2003b), the results of the PCA can be used more directly for mixing analysis to identify the sources of samples in terms of end members identified from the PC score plots.

Clearly, and as demonstrated by Christophersen and Hooper (1992) and Worrall et al (2003b), the identification of stream samples as true end members in this manner is likely to be an exaggeration – true end members in terms of the water sources would be more likely to be sources such as peat soil water and limestone groundwater, neither of which were directly sampled in this study. This is reinforced by the more detailed analysis of the PCs in terms of contrasting water sources that was provided in section 5.5. However it should be emphasised that the key purpose of this study is to relate the composition of the water from various stream and river sites, and in particular to relate the composition of the water at Broken Scar to a range of streams of differing characteristics in order to identify the relative contributions of each to, in particular, the colour at Broken Scar.

Although Christophersen and Hooper (1992) accepted that PCA can be used successfully for EMMA if enough sampling is done to ensure that all conditions and sources are covered, these constraints were not met by this study. Nonetheless, despite the limitation of PCA for end-member analysis outlined by Christophersen and Hooper (1992) and described in Chapter 3, it is a useful technique for this particular study, because in the streams sampled there are clear end-member candidates. Langley Beck is an alkaline, lowland stream with no peat cover and high ground-water influence. Rennygill Sike is a small, second-order upland catchment with consistently high colour loads and almost complete peat cover within the catchment. It is hypothesised that waters from these streams provide end-members by which the river waters can be described, even if these are not true end-members in terms of water sources. If the PCA analysis suggests end-members with similar compositions to these streamwaters then this will agree with the hypothesis and suggest that the end-members identified by PCA are appropriate. Therefore the identification of extreme streams as end members is appropriate even if they are not true end members in terms of the sources of various water characteristics.

The plot of PC1 vs PC3 (Figure 5.10) shows a general triangular distribution, suggesting three end members. Although not all samples lie completely within the ternary plot bounded by three end members, those that do not were from a sampling run that has been illustrated to show different behaviour, and so the consideration of these samples separately is reasonable. The three end members selected were Langley Beck (7th run), Rennygill Sike (7th run), and precipitation (09/12/2004). The choice of Langley Beck sample from runs 3, 6 and 7 was a somewhat subjective decision; the sample from run 7 was selected as it had the most extreme PC1 score and because many samples from run 6 scored highly on PC1 due to the anomalously high Na concentrations in this run discussed in section 5.3.1.

Furthermore although no groundwater or soil water was directly sampled, a number of peatland grips were extensively sampled in another part of this study. Samples from one of these grips when plotted against the same PC loadings exhibited trends largely similar to, but more extreme than, slightly larger peatland streams such as Rennygill Sike. Although the results of this have not been further analysed here (due to the extremely high leverage of these points in one direction, given their more extreme nature, and the lack of samples from sites close to other end members such as groundwater) this confirms the use of Langley Beck and Rennygill Sike as "effective" end members.

Solute ($mg\ l^{-1}$)	A (Langley Beck)	B (Rennygill Sike)	R (Rainfall)
Al	0.00	0.24	0.00
Ca	74.76	6.30	0.04
Fe	0.00	1.48	0.00
K	6.96	0.17	0.35
Mg	16.40	0.89	0.16
Na	21.33	3.92	2.09
Si	3.71	0.82	0.00
DOC	4.92	48.24	0.00

Table 5.8 Compositions of the end members selected from the PC1/PC2 plot

The triangular region bounded by the three selected samples is illustrated by the bold lines in Figure 5.19. The three end members are labelled as A (Langley Beck), B (Rennygill Sike), and R (rainwater). Given the interpretation of PC2 as a general concentration component (section 5.4.1), this plot can be interpreted as showing samples evolving from a single "pure" (low concentration) precipitation source. Furthermore given the interpretation of PC1 as distinguishing between samples from peat sources and those from some other evolved source (section 5.4.1), the low absolute scores of the precipitation source on PC1 relative to those for the other two proposed end members are also as expected. Therefore the evolution of samples from rainwater can be described in terms of a combination of two trends: trend R-A and trend R-B (Figure 5.19).

In a ternary mixing diagram, the trend between any two end members represents a linear combination of those end members: for a sample lying on the trend A-B the relative proportions of each end member are given by the position on the trend of the sample; a sample lying 25% along the trend from A towards B is composed of 75% A and 25% B. This description applies for each of the three bounding trends AB, RA, and RB and so samples containing a proportion of all three end members will not lie precisely on a trend but rather within the ternary plot. The composition of samples relative to the three end members can then be solved geometrically from the mixing plot, as illustrated in Figure 5.19 for a sample from the Greta, indicated as P. The proportion of evolution towards either end member A or B can be gauged by projecting a line from the source (R) in the direction of evolution of the sample through to the trend AB, intersecting the trend at point X (Figure 5.19). The relative lengths of AX and BX will then give the proportions of the evolved water in the sample that is of composition A and B respectively. Similarly the position of the sample P along the trend RX defines the extent to which the sample has evolved from source water, with RP and PX representing the proportions of source / evolved water in the sample. The overall proportions of the three end members in the sample P are then given by AX*PX, BX*PX, and RP for end member A, B and R respectively.

Since such an analysis is in terms of end members, the compositions of any samples falling outside the triangle ABR are not defined – Worrall et al (2003b) used this fact to infer the presence of an unsampled end member causing some samples to fall outside the observed trends. In this case, the samples falling outside the triangle ABR are those described earlier, chiefly from sample run 4. Whilst this does imply that the observed Langley Beck sample A does not represent a true end member for extreme baseflow conditions, the samples which are bounded by these end members represent the majority of runoff conditions and given the position of run 4 samples below the AR trend, had Langley Beck been sampled on this day it seems reasonable that the relative position of the trends would be similar.

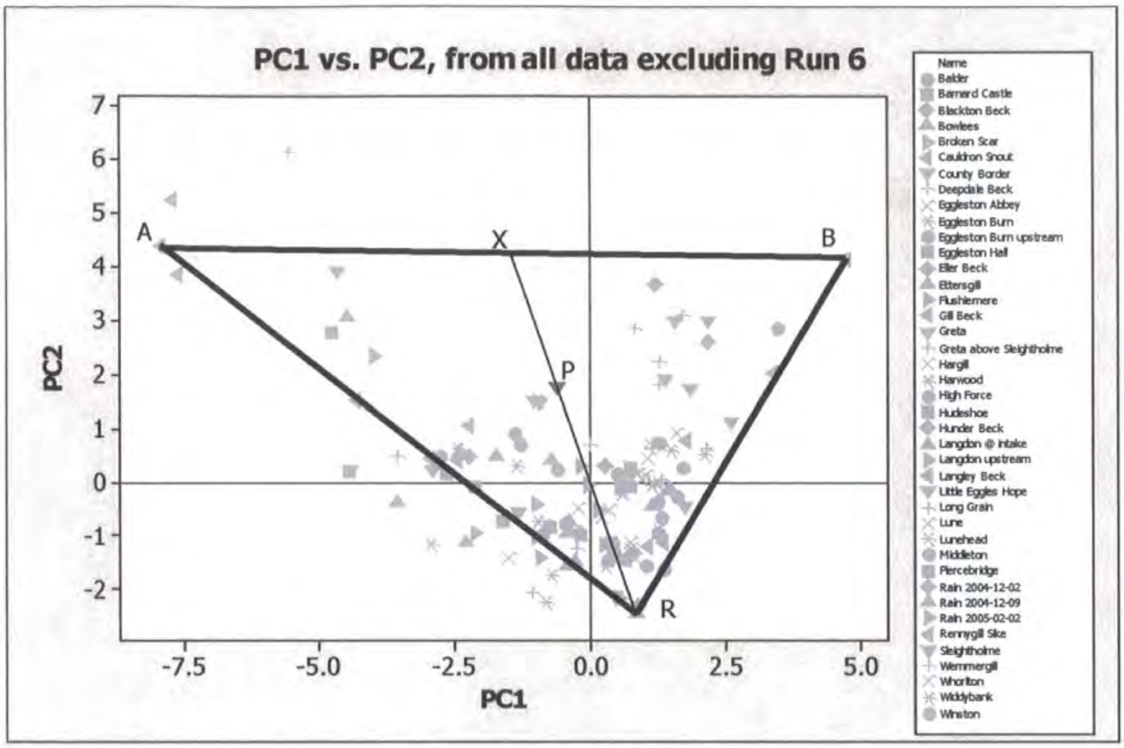


Figure 5.19 Plot of PC1 vs. PC2, showing the distribution bounded by the end members and the distances used to calculate composition for a sample P

Following this method, the composition of all the samples was calculated in terms of the three end-members A, B and R. Results are shown in Table 5.9, where catchment identification numbers are as given in Table 5.1.

		Proportion		
Catchment id	*N sampled*	*Rain*	*End member A*	*End member B*
1	7	0.650	0.241	0.109
2	3	0.724	0.142	0.134
3	4	0.091	0.890	0.019
4	3	0.732	0.137	0.131
5	2	0.706	0.093	0.201
6	6	0.420	0.386	0.194
7	3	0.547	0.406	0.047
8	1	0.591	0.169	0.239
9	4	0.720	0.112	0.168
10	3	0.762	0.113	0.125
11	5	0.608	0.170	0.222
12	2	0.726	0.107	0.167
13	2	0.579	0.273	0.148
14	2	0.392	0.218	0.390
15	3	0.518	0.221	0.261
16	7	0.723	0.096	0.180
17	5	0.574	0.444	0.000
18	6	0.686	0.115	0.199
19	5	0.638	0.119	0.243
20	2	0.538	0.080	0.382
21	6	0.780	0.177	0.043
22	3	0.792	0.033	0.175
23	3	0.565	0.288	0.147
24	4	0.727	0.249	0.024
25	3	0.898	0.075	0.028
26	2	0.807	0.031	0.161
27	3	0.589	0.060	0.351
28	1	0.853	0.187	-0.041
30	4	0.167	0.452	0.382
31	3	0.323	0.253	0.425
32	3	0.397	0.185	0.418
33	4	0.766	0.113	0.121
34	3	0.648	0.158	0.195
35	3	0.278	0.028	0.694
36	4	0.601	0.356	0.044
38	2	0.158	0.192	0.649
41	1	0.785	0.299	0.000
42	1	0.567	0.376	0.058
99	2	0.971	0.019	0.010

Table 5.9 Mean end-member composition of samples from each site

5.7 Spatial distribution of source water types

5.7.1 Direct analysis of end member compositions

The mean component composition for each site across the runs in which it was sampled is shown on the catchment schematic diagram in Figure 5.20, allowing visualisation of catchments dominated by each end member and a general impression of the mixing behaviour. Moving downstream, the composition of the River Tees gradually decreases in the rainwater end member relative to the two old-water end members. Furthermore the influence of specific tributary catchments in this change can be noted. For example, comparing the river Tees at High Force (site 22) and Middleton (site 16) clearly shows the influence of the end member A-rich Ettersgill (site 36) and Bowlees Beck (site 21), an effect that is strengthened at the next stage downstream (Tees at Eggleston Hall, site 12) where the effect of the large Hudeshoe Beck tributary (site 17) on the overall end member A proportion can be seen.

Only two sampled catchments had an overall majority of end member B: Rennygill Sike (site 35) and Hunder Beck (site 38); these are both largely flat, drained peat catchments and so their high end member B composition is as would be expected. In the initial sampling, the Eggleston Burn Upstream (site 15) and Little Eggles Hope (site 14) were noted to have high DOC levels compared with most other catchments in the north of the study area; Blackton Beck (site 42) was therefore originally selected for catchment characteristics that were predicted by the preliminary model (section 4.7) to result in lower DOC concentrations than the rest of the Eggleston Burn catchment. This selection is confirmed by the higher proportion of end member A and lower proportion of end member B noted here.

The catchment schematic does show that the catchments showing a significant influence from end member B are largely the peatland catchments in the south of the study area, and those significantly influenced by end member A are largely in the north. However, this observation regarding site 42 helps to demonstrate, along with Crook Burn (site 27), that the general north / south divide is not inherent on the catchment positions to the north or south of the river nor on their aspect, but rather on the factors identified in the modelling in chapter 4 (e.g. peat cover, slope, and drainage management). Furthermore, the work in chapter 4 distinguished DOC-rich from DOC-poor water, with no attempt to classify the latter based on source. Here it can be seen that the difference between the high and low DOC catchments is largely in terms of the proportion of end member B; the proportion of end member A does not decrease in line with increases of end member B. For example many high-DOC catchments in the south are also high in end member A (e.g. 30 and 31, the Greta and Sleightholme Beck above their confluence, and 38, Hunder Beck).

Therefore in addition to being distinguished by DOC levels (related to end member B and to catchment characteristics including peat cover), there is a second distinction to be made between catchments based on their proportion of old vs. new water, which is not related in the same way to these catchment characteristics. The catchment characteristics identified previously are related to end member B and DOC concentration, rather than to an overall proportion of old vs. new water; there is another old water observed in these catchments (represented by end member A) which is not well described by the same catchment characteristics.

Figure 5.21 shows the same sample characterisation pie charts but plotted spatially over the scale map of the overall catchment. In the absence of suitable flow data as a scaling variable, pie chart size is shown proportional to Strahler order of the catchment (note the nesting of the catchments, so each pie chart applies to the entire catchment area above the catchment in which it is shown). Here the end member compositions of the River Tees at Cauldron Snout (26), High Force (22), and Middleton (16) are instructive. The proportion of end member A in the Tees at Cauldron Snout is very low. The catchment above this point is largely peat covered and there are no significant tributaries found to be high in end member A. However at High Force the catchment includes Langdon Beck (23/28) and Harwood Beck (24), both of which are substantial tributaries with a significant end member A composition – but the proportion of end member A in the Tees is still low. This could be due to the contribution of Maize Beck (39), which unfortunately was not sampled in this part of the study. Maize Beck is also a substantial tributary with a largely peat-covered catchment with high observed DOC (in chapter 4). This water would therefore seem likely to be high in end member B, and so the relative contributions of Maize Beck and Langdon Beck / Harwood Beck may to a certain extent cancel.

5.7.2 Standardisation for inter-run variation

One potential problem with the analysis above stems from the way in which each sampling site was sampled on a different combination of days. Since there were systematic differences in the distribution of water sources (in terms of PC end member mixing) between days (Figure 5.13 - Figure 5.15) this could potentially skew the results.

One possible way of mitigating this is to normalise the results from each run relative to one another. This was achieved as follows: firstly, for each run the mean proportion of each of the three end members was calculated. Secondly, for each end member the run with the highest mean score was then identified and this score was divided by the mean score for each of the other runs in order to generate a "normalisation factor" for each end member and run. Each sample end member proportion was then multiplied by the relevant normalisation factor for its run. The results of this process are shown as a schematic and a map in Figure 5.22 and Figure 5.23 respectively.

One difference notable in the normalised data maps is a more obvious downstream evolution of the water in the River Tees towards an increasing proportion of composition A, accompanied by decreases in the proportion of both compositions R and B. The decreasing proportion of composition R represents a shift from new to old water, as would be expected moving down a catchment. Among the smaller side catchments the proportion of new water is higher among the steeper catchments: e.g. 24, 28, 36, and 41 in the north, and 19, 33, and 34 in the south; these latter catchments can be contrasted with others which have lower slope such as 38, 32 and 3. Although the flatter catchments vary in type of old water, they all have a higher proportion of old water relative to new, emphasising the faster runoff production from steeper terrain.

Another difference on the normalised data maps can be seen in the proportions of end member B, which is important given the strong loading of DOC on this composition. The highest proportions of this composition are observed at sites 35, 27, 14 and 38 (in descending order). These are among the smallest, lowest-order catchments in the study (all with Strahler order 2 or 3), and all have peat cover > 90%. Table 5.10 is sorted by fraction of peat cover and shows these catchments in comparison with the others. Of the other catchments with peat cover > 90% (but lower end member B proportions) numbers 34, 28, 33 and 15 all have substantially higher mean slope whilst 20 has a high proportion of ungripped peat. All this points to the same conclusions suggested in chapter 4: that DOC production is primarily from small, flat, low order peatland catchments, especially where there is extensive drainage.

Site number	Strahler order	Area (km^2)	Peat fraction	FP ungripped	Slope mean (deg)	Proportion B (norm)
34	3	7.6	0.97	0.89	6.11	0.16
38	3	7.4	0.95	0.74	3.66	0.49
14	3	5.5	0.95	0.95	5.81	0.55
35	2	1.7	0.95	0.16	3.86	0.63
28	4	6.5	0.95	0.86	6.92	0.00
15	3	12.7	0.92	0.88	7.16	0.24
20	3	5.9	0.92	0.88	5.85	0.28
33	4	22.4	0.92	0.83	6.31	0.11
19	4	14.2	0.91	0.65	4.73	0.21
27	2	1.1	0.91	0.76	4.83	0.60
26	5	58.8	0.89	0.90	4.77	0.36
22	6	165.0	0.87	0.90	5.52	0.33
23	4	12.6	0.86	0.89	6.75	0.17
13	4	31.4	0.85	0.93	6.82	0.13
24	4	24.9	0.85	0.94	6.33	0.07
8	4	9.5	0.85	0.91	3.83	0.17
25	1	0.5	0.84	0.95	3.38	0.06
42	3	3.2	0.83	1.00	5.87	0.22
31	4	26.9	0.83	0.74	3.28	0.33
21	4	13.1	0.83	0.81	6.63	0.05
30	4	31.8	0.82	0.87	3.15	0.34
16	6	214.0	0.81	0.89	5.74	0.25
41	3	4.9	0.81	0.84	7.56	0.00
18	5	85.9	0.80	0.75	5.36	0.25
32	3	24.1	0.77	0.88	2.42	0.34
12	6	365.0	0.77	0.86	5.86	0.27
10	6	502.0	0.69	0.85	5.24	0.22
9	6	513.0	0.67	0.85	5.19	0.23
17	3	17.5	0.67	0.96	8.63	0.02
11	4	54.9	0.66	0.74	3.87	0.25
5	6	649.0	0.65	0.86	4.86	0.30
4	6	664.0	0.64	0.86	4.81	0.22
6	5	119.0	0.63	0.87	3.74	0.18
2	6	757.0	0.57	0.86	4.57	0.21
36	3	7.9	0.56	0.62	6.01	0.06
1	6	840.0	0.52	0.86	4.26	0.14
7	4	17.1	0.47	1.00	5.11	0.05
3	5	72.3	0.07	1.00	2.96	0.03

Table 5.10 Table showing some characteristics of catchments high in end-member B, compared to other catchments.

Dark green = high B. Light green = lower B low-order catchment. Grey = all other catchments.

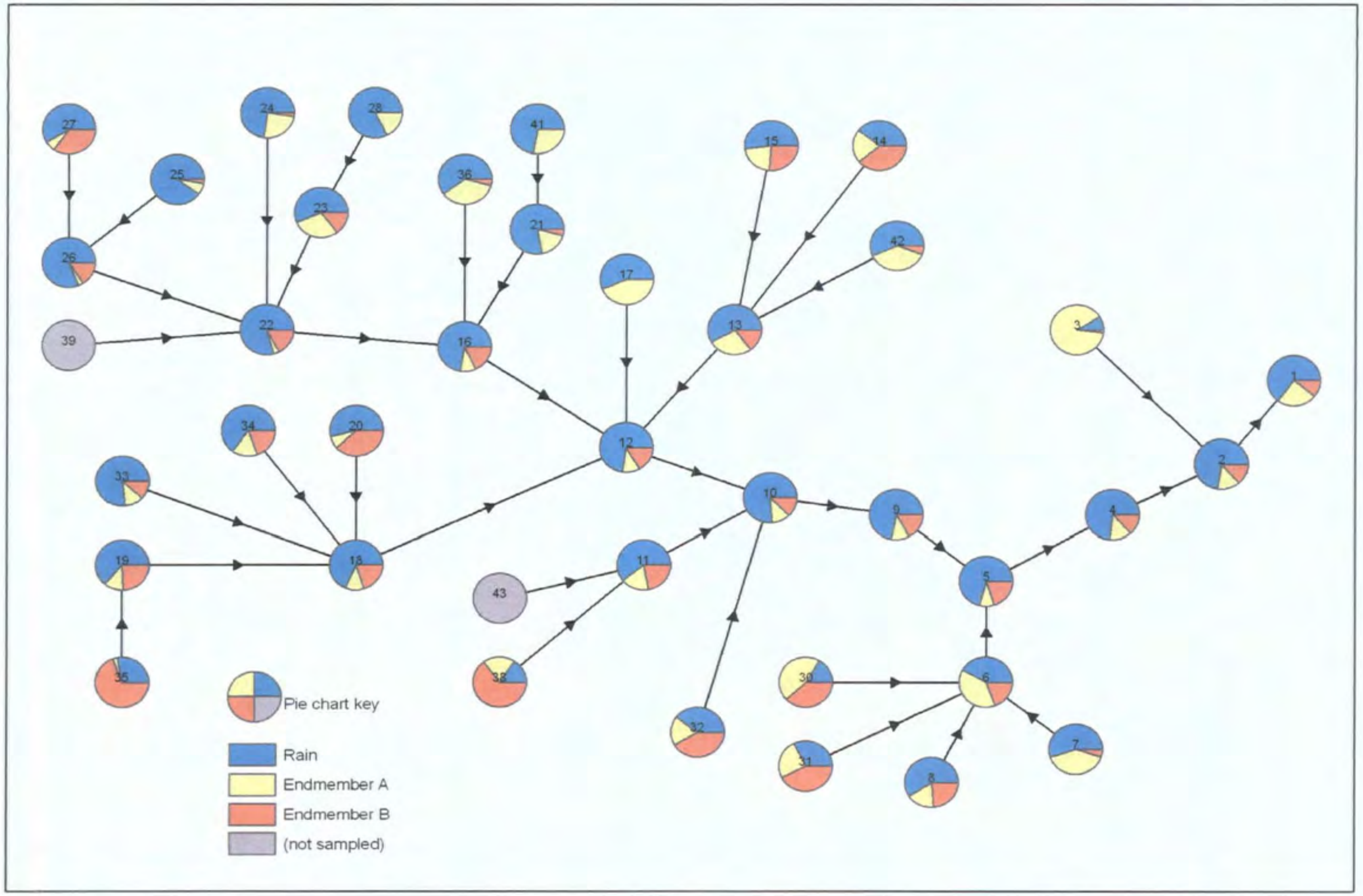


Figure 5.20 Catchment schematic showing mean end member proportions observed at each site

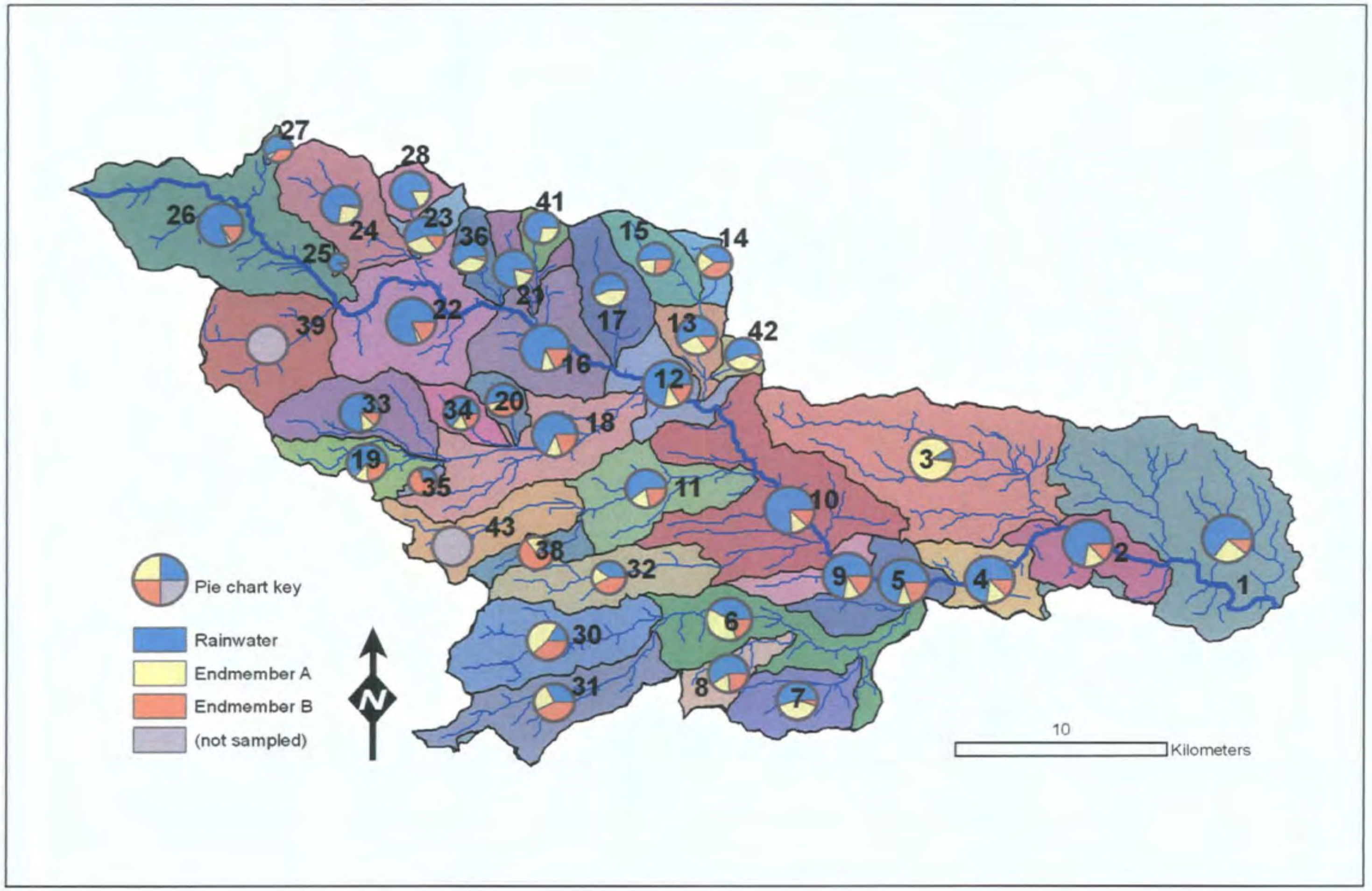


Figure 5.21 Catchment map showing mean end member proportions observed at each site; charts are sized proportional to Strahler order

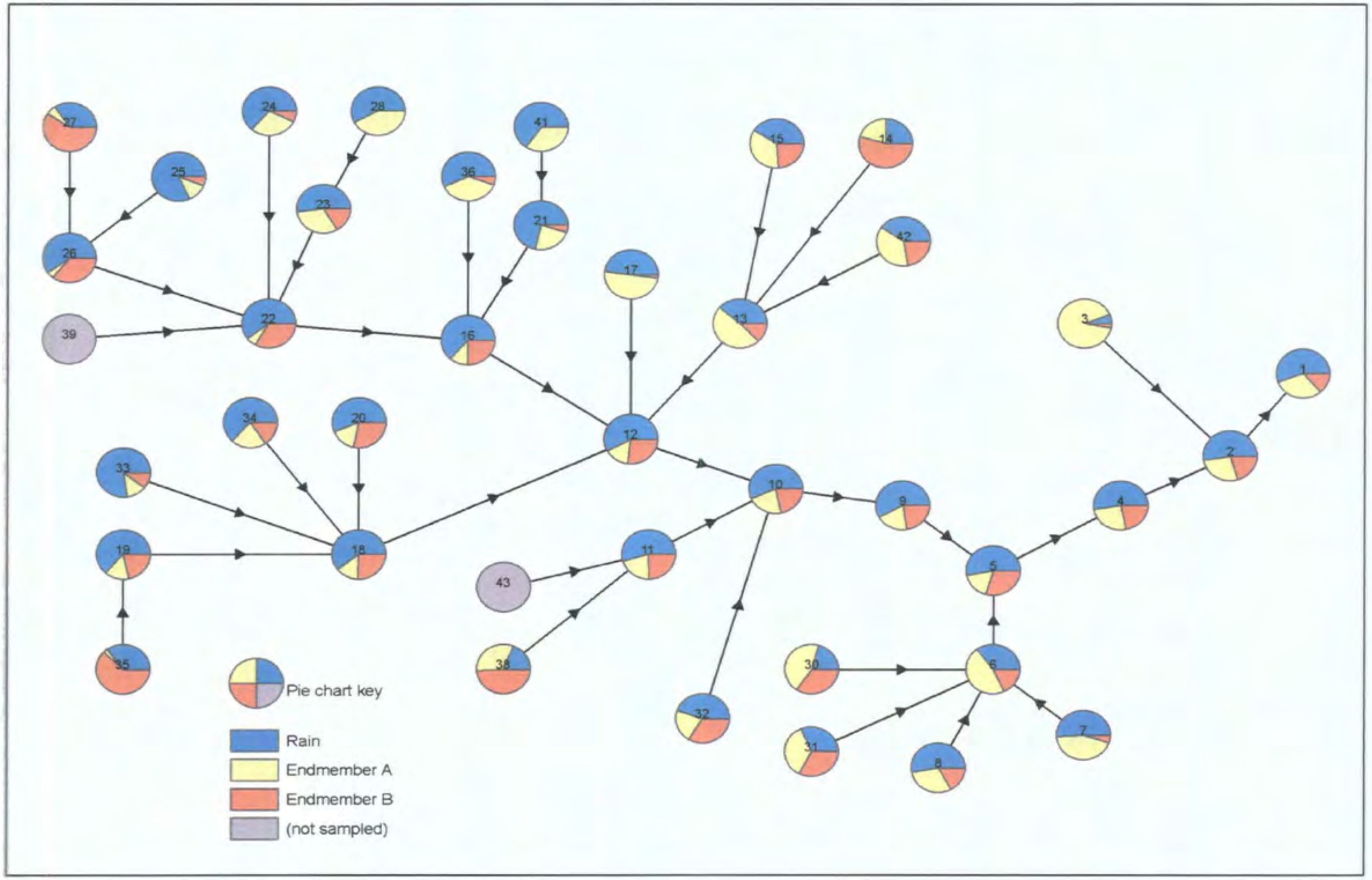


Figure 5.22 Catchment schematic showing mean end member proportions observed at each site, normalised for differences between sampling runs

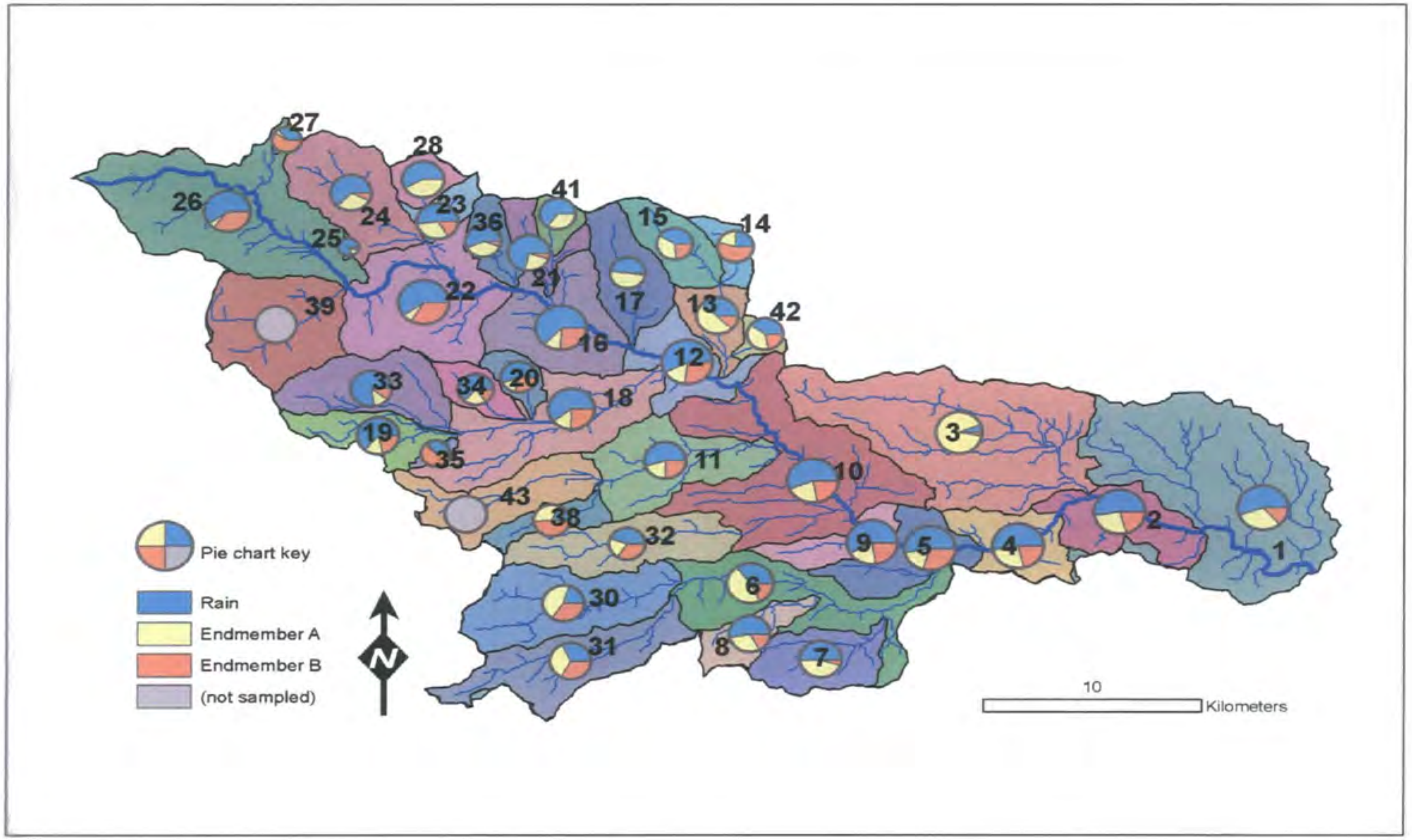


Figure 5.23 Catchment map showing mean end member proportions at each site, normalised for differences between sampling runs; charts are sized proportional to Strahler order

5.8 Summary

This chapter has used solute concentration data from samples taken across a range of conditions from sites around the Tees catchment to conduct a principal components analysis. The results of this PCA were analysed in several different ways to make inferences about the overall behaviour of the catchments and to identify water sources.

5.8.1 Component loadings

Firstly, the variable loading structure of the components was examined in order to assess how each component provided contrast between different sample characteristics (section 5.4.2). The first component contrasted peat / non-peat source waters, while the second component was found to describe general concentration and the third was suggested to contrast groundwater / non-groundwater sources (specifically, a limestone influence, given the dominant Ca loading of component 3). This was used in conjunction with sample score plots in order to identify sample groupings and trends. Identification of groupings enabled systematic differences between different sampling runs to be observed, and trends in sample scores together with knowledge of site and catchment characteristics enabled some basic inferences to be made regarding the interactions between sites. For instance, the fourth sampling run was observed to have greatly different PC3 scores to the other runs; the fact that these samples were taken under baseflow conditions was used to confirm the description of PC3 as a groundwater component.

5.8.2 Spatial analysis of component evolution

Secondly, component scores were described relative to spatial location on the main river branch (section 5.5). The nested nature of the catchments described by these samples enabled the trends to be interpreted in terms of the development of water as it moves down the catchment, whilst the fact that each of the sample sets was collected under different flow regimes enabled some suggestions to be made regarding how these development trends vary with hydrograph stage. The river sample scores on PC1 were generally higher under high-flow conditions; the loadings of PC1 translate this as representing a greater influence from peat surface sources under such conditions. This was shown to imply that during wet periods near surface runoff is more increased from peat catchments than from other catchments, and this is unlikely to be related to catchment slope. This is in line with general characterisations of peatland catchments as possessing a flashy hydrograph nature, responding more quickly to storm events than other source areas.

For PC2, comparing river sample scores between runs 2 and 3 showed a possible greater influence from infiltration-excess overland flow immediately following a dry period compared to after a longer wetting-up period, which points towards the effect of dessication on soils. PC2 scores (overall concentrations) may therefore remain lower during storms immediately following a dry period, with any flush not occurring until the source materials have wetted up.

PC2 river scores during dry conditions (run 4) did suggest that the groundwater contribution to samples may be reasonably uniform throughout the catchment, including in the more flashy, peat-dominated upper areas; however, this suggestion was not robust given the considerable scatter in only 4 samples that may have been obscuring a trend, and the possibility for high PC2 scores to result from several different sources which need not be the same throughout the catchment. Low overall scores on PC2 during run 4, compared to generally high scores on PC2 for Langley Beck, were shown to suggest that Langley Beck does not represent a "baseflow" end member but rather an end member from some different source.

The downstream trend in PC3 during the fourth run together with the lower overall PC3 scores during baseflow conditions were used to suggest that the component contrasts two types of baseflow: from peatland streams vs. mineral / rock influenced streams. Under overall baseflow conditions (run 4) PC3 decreased downstream, but under all other conditions there was no significant trend, as would be expected were the baseflow signal swamped by the influence of other sources under high flow conditions.

5.8.3 Mixing analysis from PCA scores

Finally the PC score plots were used to geometrically determine mixing proportions for each sample relative to three samples selected as "end members". The principal components score plots indicated this to be the appropriate number of end members to describe the source water types across the catchment. By plotting the end member proportions on a schematic or map of the catchment a visual impression of the mixing behaviour could be developed, which was clearer when the results for each catchment were normalised in an attempt to take account of the general differences between sampling runs. Generally the effect of large tributaries combining can be seen to combine downstream of the confluence, for example the increased end member A proportion from site 22 to site 16, due to the contribution of high-A tributaries such as 36 and 21. The proportion of "new" water (represented by the end member R) decreases downstream along the main river branch. Key sources of end member B are the smallest, peat covered, flat catchments; as end member B is strongly associated with DOC concentration this confirms the nature of DOC source areas. Overall there is nothing in these results to suggest that the three end members do not mix reasonably conservatively, but to accurately determine whether the downstream trends in end member proportions are due to evolution or mixing would require flow records for each site. With reference to DOC, in-stream processing is known to reduce concentrations downstream (e.g. Dawson et al, 2001), implying that in reality there is a non-conservative mixing which would be difficult to address here without more information on flow rates and residence times. However Dawson et al (2001) found this to be of secondary importance to spatial differences in inputs resulting from different soil types, even in summer when in-stream processing would be highest. Therefore in this study from the perspective of DOC source identification the key characteristics of source areas can be readily identified; as can low-DOC source areas, demonstrating the use of multivariate analysis to make detailed inferences about a wide range of catchment behaviours, and confirming the source areas above Broken Scar identified in chapter 4.

6 Conclusions

6.1 Introduction

This chapter presents the main conclusions of the work, specific to each objective outlined in Chapter 1. The correspondence of results obtained at the two main scales of monitoring is discussed in context of the water colour levels observed at the Broken Scar water treatment works. Limitations of the findings are discussed along with recommendations for future work.

6.1.1 Review of aims

Several specific objectives for the study were outlined in Chapter 1. These were:

1. To conduct an intensive monitoring programme of several peat drains which have a range of management treatments, and to use the results of this programme to create detailed export budgets for the drains. The operation and results of this programme were described in chapter 2.

2. To examine the differences in behaviour between the drains and determine to what extent such differences are due to blocking. This was addressed in chapters 2 and 3, based on a long term detailed monitoring programme of the five drains in addition to several other short term experiments.

3. To identify key source areas of water colour throughout the catchment of the River Tees above Broken Scar in order to describe those areas chiefly responsible for the problematic increase in water colour at Broken Scar. The sampling programme described in chapter 4 was conducted to identify these areas, and the work in chapter 5 traced these sources further through further analysis of the samples.

4. To relate the presence of such source areas to their spatial characteristics including both catchment morphology and management techniques such as drainage. Chapter 4 presented the results of this modelling.

5. To review the statistical methods used in this latter form of spatial catchment modelling, and compare the results and reliability of several such statistical

techniques. The modelling in chapter 4 was conducted following several different statistical techniques and the results of these were compared to one another and to those of previous studies in the field.

6.2 Overall conclusions

6.2.1 Objective 1

This objective was addressed in chapter 2, which described a monitoring campaign which sought to calculate the DOC export from each site, through continuous monitoring of the flow from each catchment and frequent sampling of the absorbance. Difficulties with keeping the flow monitoring equipment operational led to the application of a unit hydrograph based method to fill in the resultant gaps in the flow record; this was found to be a largely satisfactory method of modelling flow in such small catchments. Even when the hydrograph resolution was reduced to a scale that was somewhat coarse compared to the flashy nature of the hydrographs this had only minimal effect on the resultant budget calculations, showing that there is little benefit gained by continuous or quasi-continuous monitoring of flow if the corresponding concentration variable for budget calculation is not also monitored with the same level of detail.

The export budgets did show some evidence that DOC export per unit catchment area is lower from blocked grips, although this was not consistent over the period of the study. Both blocked and unblocked grips showed higher export per unit area than a pristine first order stream, which in turn was higher than a larger peatland stream. That is, all drained catchments, whether unblocked, recently blocked, or blocked over a decade ago, still exhibited higher DOC export per unit area than the natural catchments.

A recent study by Wallage et al (2006) suggested some evidence that both DOC and absorbance values may be lower in blocked drain catchments than in pristine catchments; that study, however, pertained to soil water concentrations rather than export values. This study, concerned with export from the catchments rather than concentrations in the soil water, suggested that the key driver of differences in the export was hydrological differences between the grips. The unblocked catchment was found to have a significantly higher DOC export for a given water yield than any of the blocked catchments, which in turn all had a significantly higher DOC export for a given water yield than either of the natural catchments. Holden et al (2006) showed that drainage increases throughflow relative to overland flow. From these data it is suggested that of the drained catchments, the unblocked catchment has the greatest access to DOC produced in the soil, implying a greater proportion of throughflow. These data also show that while blocking may reduce this throughflow proportion, possibly through raising of the water table causing a greater proportion of runoff to be saturation-excess overland flow, it seems unlikely to do so to such an extent as to return the catchment to a natural state.

6.2.2 Objective 2

Following identification in chapter 2 of differences in the DOC export of the drains, chapter 3 addressed objective 2 by examining the differences between the grips in more detail. Comparing the relationship between pH and conductivity, measured on a large number of samples taken across a wide range of flow conditions, showed a consistent negative (increasing conductivity vs. decreasing pH) relationship between the artificially drained sites, the coefficient of which was significantly different only in one of the blocked sites and even then not by a large amount; the coefficient of the relationship was also not significantly different from that of rainwater. This was interpreted as showing that each grip samples water which has developed along a common pathway from a single source – these development pathways do not differ between the grips. This finding is in contrast with studies in the literature which show a positive trend (increasing conductivity / increasing pH) – for example Sjörs and Gunnarsson (2002) showed a positive trend in samples collected from a range of peat surface pools in Sweden. Such a trend is indicative of chemical interaction between the peat and water and since it is not observed in these data, it would appear that the export of these catchments is not well connected to the peat chemistry. The single trend observed here represents an increasing concentration, and the pH intercept of the trend together with the correspondence of the trend in the rainwater samples suggests that the increasing trend of increasing concentration is from a single rainwater source, which is not altered in any way that differs between the grips.

The quasi-continuous monitoring of flow in two of the grips, one blocked and one unblocked, was augmented with conductivity monitoring at the same resolution, enabling an analysis of the intra-storm behaviour of these catchments through examination of conductivity vs. flow hysteresis loops. Since it had been shown that high conductivity had a common cause in these two grips, namely older and deeper water, this was effectively a comparison of the distribution of old and new water in the storm runoff of the grips. The blocked grip (Hexham 3) had generally lower conductivity, representing a smaller proportion of old (soil) water in the runoff. Although the behaviour in events varied, possibly due to varying infiltration capacity, the key differences observed between the grips were this lower concentration in the blocked grip, together with a greater tendency to step changes in the conductivity. The conclusion from this is that the pools formed behind the block dams in Hexham 3 have a substantial buffering effect that makes interpretation of the catchment runoff difficult, but also that it seems likely that the differences are attributable to a generally shallower depth of sampling in Hexham 3. This may be due to a greater proportion of overland flow in Hexham 3 following rising of the water table following blocking – a desirable result in terms of lowering DOC export – but it may be nothing more than physical differences between the two grips if Hexham 3 is shallower.

Grab samples from all the sites were analysed for base metal cations and these results were used to conduct a multivariate analysis with the aim of identifying mixing end-members and testing whether these differed between the grips. There appeared to be a common trend in the grips which paralleled the trend in rainwater composition (figure 3.27), which although not conclusive would agree with the results from the pH vs. conductivity analysis described above. Although such a trend represented a major effect in the data, the sites were not significantly separated from one another by it. Mixing end members could not be unambiguously identified in the data, but selecting as end members those samples which circumscribed most grip samples enabled a general analysis to be undertaken. The end member which was related to the composition of high-DOC runoff (end member B – section 3.4.8) did identify significant differences between the unblocked grip and the blocked grips. Once again this showed that the unblocked grip contains a higher proportion of deeper water, a difference which is sustained over a wider range of conditions. However as with the hysteresis analysis, this cannot be said with certainty to represent anything more than physical differences in the depth of the grips.

Finally a tracer experiment confirmed the importance to the catchment export of the pools behind the block dams. The tracer was observed in two separate pulses in each grip – these may be due to two different transport processes within the soils, but the only differences between the grips seemed to be explained by the hypothesis of retardation in the pools.

In summary, the conclusions relative to objective 2 are that the export of the unblocked grip is higher than that of the blocked grips in both DOC and overall concentration, but this does not imply differences between the catchments in either the rate or extent of production of DOC and other solutes. Rather, the effect of blocking is to reduce the overall concentration and quantity of the dissolved export through alteration of the hydrological behaviour of the catchments.

6.2.3 Objective 3

This objective was addressed in chapters 4 and 5. A series of grab sampling campaigns from sites around the Broken Scar catchment were conducted and the samples were analysed for DOC concentration along with concentration of base metal cations. The catchments of each of the sampling sites were identified and mapped, and it was observed that there was a general divide between high DOC water in the south of the Broken Scar catchment, and low DOC water to the north. Areas with particularly high concentrations included the catchments of the Rivers Greta, Balder, and Lune. The work in chapter 5 took a different approach to identifying the DOC sources through principal components analysis and mixing analysis. Three end members were identified, representing three fundamental source water types that were identified in the catchment: rainwater, groundwater, and peat runoff. The nested nature of sampling sites along the Tees allowed the development of the river to be described in terms of these three influences, illustrating the greater storm runoff that occurs from peat areas along with the decreasing proportion of peat influence down the catchment, as would be expected as the fraction of catchment peat cover decreases. Three end members were identified in the mixing analysis which indicated three fundamental source water types within the catchment: these were attributed (based on the sites from which they were collected) to rainwater, peat runoff, and another "old" water, probably groundwater. Mapping of the distribution of these end members confirmed that the proportion of new (rain) water decreased down the catchment, and the relative proportions of the two old water endmembers were dependent primarily on catchment characteristics. High proportions of end member B were observed to be related to catchment characteristics in a similar way to DOC concentrations in chapter 4: low slope, high peat cover, and extensive drainage being the key factors.

6.2.4 Objective 4

This objective was addressed in chapter 4. A series of grab sampling campaigns produced samples from a wide range of subcatchments around the Broken Scar catchment, which were analysed for DOC concentration and for base metal cations; a comprehensive series of catchment statistics was also produced to describe each subcatchment. Areas with high DOC export were mapped as described under objective 3, and through the use of a range of statistical regression techniques were related to catchment characteristics, enabling the generation of predictive maps of DOC export from a greater range of sites. The range of statistical methods used was greater than in previous studies, allowing comparison of the results as described under objective 5. A binary logistic regression approach was also introduced to identify specifically areas which either contribute towards or dilute the colour at Broken Scar.

Relating DOC concentration to catchment characteristics is an approach that has been taken by several previous studies, as discussed in section 4.2, with varying results. The results of the study in chapter 4 showed that the catchment characteristics which were strongly related to DOC concentration were in good agreement with those found in previous studies: extent of peat cover, shallow slope, and high elevation, along with the extent of drained and burned areas in the peatland; the statistically rigorous approach of this study enables the results to be treated with greater confidence than was previously appropriate. High DOC, concentrating areas were mainly in the upper catchments of the Balder, Lune, and Greta, along with the upper reaches of the Tees catchment.

6.2.5 Objective 5

This objective was addressed in chapter 4, which showed that differences in which catchment descriptors were found to be significant predictors of DOC concentration is likely to be due more than anything else to the limited suitability of the data for the statistical techniques used. This implies that the results of these studies are in agreement to a greater extent than may be assumed from the differences in specific catchment morphometrics used, with the key factors leading to increased concentrations being extensive peat cover, artificial drainage and burning, and low slope. Although factors such as peat cover and low slope are themselves correlated due to the nature of peat formation, they do also have separate effects on the resultant DOC export. These findings were strengthened by the use of partial least squares regression, a technique which has been developed in chemometrics to make robust predictions from a large and ill-conditioned set of predictor variables, yet which has not been previously applied to studies of this nature. Although the technique is not affected by the same data limitations as classical regression techniques, it still identified the same key catchment types. This means that such models can be used with reasonable confidence to identify and predict key source areas for high DOC runoff concentration, and also shows that although the data in this and many other studies do not strictly meet the requirements of the classical regression techniques used, their results are nonetheless valid.

6.2.6 General

With reference to all the above objectives, the key findings of this work can therefore be summarised as follows:

- Unblocked grips export somewhat more DOC than blocked grips. However blocked grips, even more than a decade after blocking, still export more DOC than pristine sites.

- The grip runoff shows minimal chemical interaction with the peat and so does not differ between sites in ways that cannot be attributed to different depths of runoff source.

- Therefore the differences in DOC export are driven primarily by differences in water yield from the catchments, and differences in the depth within the soil from which runoff originates, rather than by changes in the production rate of DOC. Blocking programmes should thus be designed for maximum water retention.

- Along with peat cover and catchment slope, the extent to which peat is drained or burned on a catchment wide scale is significantly related to the exported DOC concentration.

- The flashy nature of the catchment of the Tees above Broken Scar and associated low retention times means that the mixing behaviour is largely conservative: differences in DOC input are of key importance to the catchment export and in stream processing or DOC removal is of minor importance. This implies that identification of source water types and areas is indeed a useful strategy in managing catchment export.

- The water observed in streams and rivers throughout the catchment can be described in terms of three end members: peat runoff, lowland or groundwater runoff, and relatively unaltered rainwater.

6.3 Data limitations

It is acknowledged that there are some limitations inherent in the methods and data used in this study. Firstly, in terms of the analysis protocols used two points should be made. Due to the large number of samples collected in the grip sampling campaigns, it was not possible to directly analyse DOC concentrations and therefore absorbance was used as a proxy for DOC. Regular calibration experiments for this relationship were carried out and these did indicate that adoption of a single relationship across sites was appropriate for these data, but this is in contrast with recent studies on soil water from peat sites (Wallage et al, in review). The calibration should therefore be assessed more rigorously in future studies, not least to examine how far the findings of Wallage et al (in review) scale up from soil water to catchment export.

Furthermore, the analyses of grip samples, both for absorbance and directly for DOC concentration, were conducted on unfiltered samples. Although this is in contrast to common protocol, the rationale was that the study sought to compare colour and DOC export with that observed in the input river water at the Broken Scar treatment works, where DOC removal by flocculation is conducted on unfiltered water. The greater number of samples that could be analysed here without the additional step of filtration, allowing the construction of more detailed export records, was therefore considered to be of greater benefit. Nonetheless to address this concern a limited number of samples from each site were filtered, and it was observed that membrane filters clogged extremely quickly and after capturing only extremely small quantities of sediment (of the order of 1-2 mg on a standard 0.45μm, 49mm diameter filter membrane; unpublished data). This suggests that the non-dissolved matter in the samples is predominantly in the colloidal range and may act to reduce pore size in the filters, effectively causing smaller material to be captured with continued filtration. This would lead to inconsistency in the particle size to which samples were actually filtered, and as such the use of unfiltered samples may in fact ensure greater consistency. However, the implication in these results is that the term DOC should be interpreted with caution, with measurements more accurately reflecting the concentration of (DOC + colloidal suspended material).

A key finding with regard to the blocked grips was the importance of the pools behind the block dams and the retardation of water that these cause. Once again, the results of this study are presented in context of the export from the catchments, but in order to gain from these results an understanding of the changes in DOC production within the soil, it would be necessary to better understand the extent to which DOC and colour change over time within the retarded water. This would entail sampling along the length of the drain channel from the pools behind each dam, in addition to at the drain outlet as was done here.

The focus of this study on water colour at the treatment works means also that other aspects of the carbon cycle of the peatlands are not addressed. As described in chapter 1 several studies have identified changes in other aspects of the carbon budget of peats following water table rise, with CO_2 exports generally decreasing and CH_4 exports increasing. Construction of a total carbon budget for the peat is beyond the scope of this study but work towards such a goal is underway at Durham University; the data from this project will form an important component of this as DOC has been shown to be the dominant form of carbon export (e.g. Dawson et al, 2002).

A final limitation, with regard to the catchment-wide study, was in the number of sampling campaigns that were conducted. Ideally enough samples should be gathered from each site to represent the behaviour of each catchment across a range of flow and seasonal conditions. Since this was not possible in this study, the samples were instead grouped by considering the similarities in the actual sampled conditions. A study sampling a range of sites across sufficient variation in conditions to construct DOC rating curves for each site would be the next step towards a model that could be used to predict colour load at a treatment works on any one occasion from catchment spatial characteristics. Such a model would then be of utility for example in indicating the appropriate drawdown and release from reservoirs around the catchment in order to minimise colour peaks at the treatment works.

6.4 Context of the results and recommendations for future work

The findings of this study and their limitations can be used to direct a number of future research objectives. The results from the grip monitoring suggested that DOC production was fast on the inter-event timescale and that hydrological change was therefore the key driver of DOC export change. However it is intuitive that there must be a limit to this and so work is required to assess the actual speed of DOC production, as would become relevant in the case of prolonged events of low enough intensity that throughflow remained significant. The data in this study do not provide information on how or when DOC production becomes exhausted during large or prolonged events. This could be assessed through the collection of more temporally detailed data, by sampling during such events, or through laboratory-based peat core experiments.

Although this means that further work is needed to identify any changes in DOC production following blocking, grip blocking was nonetheless found to lead to differences in DOC export through hydrological change. A grip blocking programme can therefore be recommended as an appropriate strategy that will lead to the reduction of water colour at the treatment works, but the magnitude of such a reduction or the timescale over which it will remain effective cannot be identified from these data.

In order to scale up these results for individual grips to a catchment-wide effect, such as would be required to quantitatively predict the effect of a catchment-wide blocking programme on the DOC at Broken Scar or any other catchment, data will be required to answer two key questions. Firstly, the extent and density of drainage within the catchment, and secondly how the hydrological changes within individual grips affect the behaviour of a larger gripped area. Both of these are areas where there is currently a dearth of information.

With regard to the first point, the drainage extent dataset used in this study was largely empirical, without estimates of either drainage density or extent of blocking and therefore cannot be used to quantitatively apply the results found here for individual grips to a catchment-wide scale. There is no unified database of peatland drainage programmes and in the majority of cases there is no formalised record even at a catchment scale of the extent and intensity of drainage. Early steps towards creation of such a database are now being taken: a study is underway in the North Pennines by the Peatscapes group to digitise all grips and their state within the North Pennines AONB (A. Armstrong, pers. comm.).

With regard to the second point above, in the context of scaling up results from individual grips to whole gripped areas the overall change in hydrology of the peatland through gripping would also need to be monitored: Does blocking retard runoff from the peatland as a whole, or merely divert it from the individual blocked grips to other runoff pathways? Recent work by Holden et al (2006) illustrated the effect that drainage within a catchment can have on the flow leaving the catchment, increasing the flashy nature of the hydrograph. However, as yet no work has assessed the extent to which blocking can reverse this on a river-wide scale. If water is retarded by blocks across a dense drainage network, it seems likely that a point will be reached where a proportion of that water leaves the catchment by other means. The magnitude of such export and its partitioning into overland flow and throughflow is unknown and will be of crucial importance in understanding the DOC export of a drained peatland, rather than that of individual peat drains.

Bibliography

Adgar, A., C. S. Cox and C. A. Jones (2004). Enhancement of coagulation control using the streaming current detector. *Bioprocess and Biosystems Engineering* **27**(5): 349-357.

Aitkenhead, J. A., D. Hope and M. F. Billett (1999). The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrological Processes* **13**(8): 1289-1302.

Aitkenhead, J. A. and W. H. McDowell (2000). Soil C : N ratio as a predictor of annual riverine DOC flux at local and global scales. *Global Biogeochemical Cycles* **14**(1): 127-138.

Archer, D. and D. Stewart (1995). The Installation and Use of a Snow Pillow to Monitor Snow Water Equivalent. *Journal of the Chartered Institution of Water and Environmental Management* **9**(3): 221-230.

Babyak, M. A. (2004). What you see may not be what you get: A brief, nontechnical introduction to overfitting in regression-type models. *Psychosomatic Medicine* **66**(3): 411-421.

Baird, A. J. and S. W. Gaffney (2000). Solute movement in drained fen peat: a field tracer study in a Somerset (UK) wetland. *Hydrological Processes* **14**(14): 2489-2503.

Bartlett, R. J. and D. S. Ross (1988). Colorimetric Determination of Oxidizable Carbon in Acid Soil Solutions. *Soil Science Society of America Journal* **52**(4): 1191-1192.

Billett, M. F., S. M. Palmer, D. Hope, C. Deacon, R. Storeton-West, K. J. Hargreaves, C. Flechard and D. Fowler (2004). Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. *Global Biogeochemical Cycles* **18**(1): 12.

Blackith, R. E. and R. A. Reyment (1971). *Multivariate Morphometrics*. London, Academic Press.

Boorman, D. B., J. M. Hollis and A. Lilly (1995). Hydrology of soil types: a hydrologically based classification of the soils of the United Kingdom. *Institute of Hydrology Report No.126*.

Bowler, D.G. 1980: *The drainage of wet soils*. London: Hodder and Stoughton.

Branfireun, B. A. and N. T. Roulet (1998). The baseflow and storm flow hydrology of a precambrian shield headwater peatland. *Hydrological Processes* **12**(1): 57-72.

Bursill, D. (2001). Drinking water treatment – understanding the processes and meeting the challenges. *Water Science and Technology: Water Supply* **1**(1): 1-7.

Burt, T., A. L. Heathwaite and J. C. Labadz (1990). Runoff production in peat-covered catchments. *Process Studies in Hillslope Hydrology*. T. Burt and M. G. Anderson. Chichester, Wiley: 463-500.

Burt, T. P., J. K. Adamson and A. M. J. Lane (1998). Long-term rainfall and streamflow records for north central England: Putting the Environmental Change Network site at Moor House, Upper Teesdale, in context. *Hydrological Sciences Journal* **43**(5): 775-787.

Burt, T. P., J. C. Labadz and D. P. Butcher (1997). The hydrology and fluvial geomorphology of blanket peat: Implications for integrated catchment management. *Blanket Mire Degradation : Causes, Consequences and Challanges, University of Manchester, 9-11 April, 1997 : proceedings*. J. H. Tallis, R. Meade and P. D. Hulme. Aberdeen, Macauley Land Use Research Institute on behalf of the Mires Research Group: 121-127.

Campbell. (2006). "CR10X Measurement & Control Module." Retrieved 18 November, 2006, from http://www.campbellsci.co.uk/index.cfm?id=52.

Casey, H. and C. Neal (1986). Abiological controls on silica in chalk streams and groundwaters. *Sediments and Water Interactions*. P. G. Sly. New York, Springer: 332-342.

Chatfield, C. and A. J. Collins (1980). *Introduction to Multivariate Analysis*. London, Chapman and Hall.

Christophersen, N. and R. P. Hooper (1992). Multivariate-Analysis of Stream Water Chemical-Data - the Use of Principal Components-Analysis for the End-Member Mixing Problem. *Water Resources Research* **28**(1): 99-107.

Christophersen, N., C. Neal, R. P. Hooper, R. D. Vogt and S. Andersen (1990). Modeling Streamwater Chemistry as a Mixture of Soilwater End-Members - a Step Towards 2nd-Generation Acidification Models. *Journal of Hydrology* **116**(1-4): 307-320.

Clausen, J. C. (1980). The quality of runoff from natural and disturbed Minnesota peatlands. The role of peatlands in a world of limited resources, energy, food, fibre and natural areas *6th International Peat Congress*. Duluth, Minnesota, International Peat Society: 523-532.

Cohen, J. (1977). *Statistical Power Analysis for the Behavioral Sciences*. New York, Academic Press.

Cole, L., R. D. Bardgett, P. Ineson and J. K. Adamson (2002). Relationships between enchytraeid worms (Oligochaeta), climate change, and the release of dissolved organic carbon from blanket peat in northern England. *Soil Biology & Biochemistry* **34**(5): 599-607.

Cooper, A., R. Murray and T. McCann (1991) *The environmental effects of blanket peat exploitation.* Coleraine: University of Ulster.

Cooper, D. M. and C. D. Watts (2002). A comparison of river load estimation techniques: application to dissolved organic carbon. *Environmetrics* **13**(7): 733-750.

Crist, E. P. (1985). A TM Tasseled Cap Equivalent Transformation for Reflectance Factor Data. *Remote Sensing of Environment* **17**(3): 301-306.

Crist, E. P. and R. C. Cicone (1984). A Physically-Based Transformation of Thematic Mapper Data - the TM Tasseled Cap. *IEEE Transactions on Geoscience and Remote Sensing* **22**(3): 256-263.

Croke, B. F. W., F. Andrews, A. J. Jakeman, S. M. Cuddy and A. Luddy (2006). IHACRES classic plus: A redesign of the IHACRES rainfall-runoff model. *Environmental Modelling & Software* **21**(3): 426-427.

Dáil Éireann (1998) "Dáil Éireann - Volume 487 - 26 February, 1998 Written Answers. - Raised Bog Conservation". Retrieved 4th April, 2007, from http://historical-debates.oireachtas.ie/D/0487/D.0487.199802260091.html

Davies, A. M. C. (2005). Back to basics: Applications of Principal Components Analysis. *Spectroscopy Europe* **17**(2): 30-31.

Davis, S. N., G. M. Thompson, H. W. Bentley and G. Stiles (1980). Groundwater Tracers - A Short Review. *Ground Water* **18**(1): 14-23.

Dawson, J. J. C., C. Bakewell and M. F. Billett (2001). Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? *Science of the Total Environment* **265**(1-3): 153-167.

Dawson, J. J. C., M. F. Billett, C. Neal and S. Hill (2002). A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. *Journal of Hydrology* **257**(1-4): 226-246.

DEFRA. (2006, 16/11/2006). "The June Agricultural Survey." Retrieved 21 November, 2006, from http://www.defra.gov.uk/esg/work_htm/publications/cs/farmstats_web/default.htm.

Druck. (2004). "1830/1840 Series Datasheet." Retrieved 18 November, 2006, from http://www.gesensing.com/products/resources/datasheets/1830.pdf.

Eatherall, A., M. S. Warwick and S. Tolchard (2000). Identifying sources of dissolved organic carbon on the River Swale, Yorkshire. *Science of the Total Environment* **251**: 173-190.

Eckhardt, B. W. and T. R. Moore (1990). Controls on Dissolved Organic-Carbon Concentrations in Streams, Southern Quebec. *Canadian Journal of Fisheries and Aquatic Sciences* **47**(8): 1537-1544.

ECN. (2006a). "ECN Sites: Trout Beck." Retrieved 18 November, 2006, from http://www.ecn.ac.uk/sites/ecnsites.asp?site=R22.

ECN. (2006b). "ECN Sites: Moor House - Upper Teesdale." Retrieved 18 November, 2006, from http://www.ecn.ac.uk/sites/ecnsites.asp?site=T04.

Efron, B. and R. Tibshirani (1986). Bootstrap Methods for Standard Errors, Confidence Intervals, and Other Measures of Statistical Accuracy. *Statistical Science* **1**(1): 54-77.

Egglesmann, R. (1971). On the hydrological influence of a bog. *Telma* **1**(1): 37-38.

Evans, C. D., P. J. Chapman, J. M. Clark, D. T. Monteith and M. S. Cresser (2006). Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology* **12**(11): 2044-2053.

Evans, C. D., T. D. Davies, P. J. Wigington, M. Tranter and W. A. Kretser (1996). Use of factor analysis to investigate processes controlling the chemical composition of four streams in the Adirondack Mountains, New York. *Journal of Hydrology* **185**(1-4): 297-316.

Evans, C. D., D. T. Monteith and D. M. Cooper (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution* **137**(1): 55-71.

Evans, M. G., T. P. Burt, J. Holden and J. K. Adamson (1999). Runoff generation and water table fluctuations in blanket peat: evidence from UK data spanning the dry summer of 1995. *Journal of Hydrology* **221**(3-4): 141-160.

Fearing, D. A., J. Banks, S. Guyetand, C. M. Eroles, B. Jefferson, D. Wilson, P. Hillis, A. T. Campbell and S. A. Parsons (2004). Combination of ferric and MIEX (R) for the treatment of a humic rich water. *Water Research* **38**(10): 2551-2558.

Flury, M. and N. N. Wai (2003). Dyes as tracers for vadose zone hydrology. *Reviews of Geophysics* **41**(1).

Forina, M., S. Lanteri, M. C. C. Oliveros and C. P. Millan (2004). Selection of useful predictors in multivariate calibration. *Analytical and Bioanalytical Chemistry* **380**(3): 397-418.

Forsberg, C. (1992). Will an Increased Greenhouse Impact in Fennoscandia Give Rise to More Humic and Colored Lakes. *Hydrobiologia* **229**: 51-58.

Foster, J. A. and A. T. McDonald (2000). Assessing pollution risks to water supply intakes using geographical information systems (GIS). *Environmental Modelling & Software* **15**(3): 225-234.

Fraser, C. J. D., N. T. Roulet and T. R. Moore (2001). Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog. *Hydrological Processes* **15**(16): 3151-3166.

Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds and N. Fenner (2001a). Export of organic carbon from peat soils. *Nature* **412**(6849): 785-785.

Freeman, C., N. Ostle and H. Kang (2001b). An enzymic 'latch' on a global carbon store - A shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. *Nature* **409**(6817): 149-149.

Freeman, C., N. J. Ostle, N. Fenner and H. Kang (2004). A regulatory role for phenol oxidase during decomposition in peatlands. *Soil Biology & Biochemistry* **36**(10): 1663-1667.

Fuller, R. M., G. B. Groom and A. R. Jones (1994). The Land-Cover Map of Great-Britain - an Automated Classification of Landsat Thematic Mapper Data. *Photogrammetric Engineering and Remote Sensing* **60**(5): 553-562.

Gafni, A. and K. N. Brooks (1990). Hydraulic Characteristics of 4 Peatlands in Minnesota. *Canadian Journal of Soil Science* **70**(2): 239-253.

Green, S. B. (1991). How Many Subjects Does It Take to Do a Regression Analysis? *Multivariate Behavioral Research* **26**(3): 499-510.

Grieve, I. C. (1990). Seasonal, Hydrological, and Land Management Factors Controlling Dissolved Organic-Carbon Concentrations in the Loch Fleet Catchments, Southwest Scotland. *Hydrological Processes* **4**(3): 231-239.

Haag, I. and B. Westrich (2002). Processes governing river water quality identified by principal component analysis. *Hydrological Processes* **16**(16): 3113-3130.

Halderson, J. S. and D. R. Glasnapp (1972). Generalized Rules for Calculating Magnitude of an Effect in Factorial and Repeated Measures Anova Designs. *American Educational Research Journal* **9**(2): 301-310.

Harrison, R. M., G. A. Thorogood and R. F. Lacey (1990). Comparison of load estimation from grab samples and flow proportional sampling. Water Research Centre, report no. PRS 2383-M. Medmenham, UK, Water Research Centre.

Hautala, K., J. Peuravuori and K. Pihlaja (2000). Measurement of aquatic humus content by spectroscopic analyses. *Water Research* **34**(1): 246-258.

Hays, W. L. (1963). *Statistics*. New York, Holt, Rinehart and Winston.

Hildesheim, M. E., K. P. Cantor, C. F. Lynch, M. Dosemeci, J. Lubin, M. Alavanja and G. Craun (1998). Drinking water source and chlorination byproducts II. Risk of colon and rectal cancers. *Epidemiology* **9**(1): 29-35.

Hooijer, A., M. Silvius, H. Wösten, and S. Page (2006). PEAT-CO2, Assessment of CO2 emissions from drained peatlands in SE Asia. Delft Hydraulics Report Q3943 (2006).

Holden, J., N. R. Bosanko and M. Gascoign (2005). Erosion caused by surface land drains in upland peatlands and the impact of remediation strategies. *European Geophysical Union General Assembly*. Vienna, Austria, Geophysical Research Abstracts, 7.

Holden, J. and T. P. Burt (2003a). Hydrological studies on blanket peat: the significance of the acrotelm-catotelm model. *Journal of Ecology* **91**(1): 86-102.

Holden, J. and T. P. Burt (2003b). Runoff production in blanket peat covered catchments. *Water Resources Research* **39**(7): art. no.-1191.

Holden, J., P. J. Chapman and J. C. Labadz (2004). Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration. *Progress in Physical Geography* **28**(1): 95-123.

Holden, J., M. G. Evans, T. P. Burt and M. Horton (2006). Impact of land drainage on peatland hydrology. *Journal of Environmental Quality* **35**(5): 1764-1778.

Hope, D., M. F. Billett and M. S. Cresser (1994). A Review of the Export of Carbon in River Water - Fluxes and Processes. *Environmental Pollution* **84**(3): 301-324.

Hope, D., M. F. Billett, R. Milne and T. A. W. Brown (1997a). Exports of organic carbon in British rivers. *Hydrological Processes* **11**(3): 325-344.

Hope, D., M. F. Billett and M. S. Cresser (1997b). Exports of organic carbon in two river systems in NE Scotland. *Journal of Hydrology* **193**(1-4): 61-82.

Hotelling, H. (1933). Analysis of a complex of statistical variables into principal components. *Journal of Educational Psychology* **24**: 417-41, 498-520.

Ingram, H. A. P. (1967). Problems of Hydrology and Plant Distribution in Mires. *The Journal of Ecology* **55**(3): 711-724.

Ingram, H. A. P. (1978). Soil Layers in Mires - Function and Terminology. *Journal of Soil Science* **29**(2): 224-227.

ISO (1980). ISO 1438/1-1980(E): Water Flow Measurement in open channels using weirs and venturi flumes - Part 1: Thin plate weirs.

Jakeman, A. J. and G. M. Hornberger (1993). How Much Complexity Is Warranted in a Rainfall-Runoff Model. *Water Resources Research* **29**(8): 2637-2649.

Jakeman, A. J., I. G. Littlewood and H. D. Symons (1991). *Features and applications of IHACRES: A PC program for identification of unit hydrographs and component flows from rainfall, evapotranspiration and streamflow data.* 13th IMACS World Congress on Computation and Applied Mathematics, Dublin, Ireland, Criterion.

Joensuu, S, E. Ahti and M Vuollekoski (2002). Effects of Ditch Network Maintenance on the Chemistry of Run-off Water from Peatland Forests. *Scandinavian Journal of Forest Research* **17**: 238-247

Johnson, A. H. (1979). Estimating Solute Transport in Streams from Grab Samples. *Water Resources Research* **15**(5): 1224-1228.

Johnson, G. A. L. and K. Dunham (1963). *The geology of Moor House : a national nature reserve in north-east Westmorland*. London, H.M.S.O.

Joosten, H. (1997). European mires: a preliminary status report. International Mire Cons. Group Members Newsletter. 3: 10–13.

Judd, C. M. and G. H. McClelland (1989). *Data analysis: A model comparison approach*. New York, Harcourt Brace Jovanovich.

Kaufman, L. and P. J. Rousseeuw (1990). *Finding Groups in Data: an Introduction to Cluster Analysis*. New York, John Wiley and Sons.

Komulainen, V. M., E. S. Tuittila, H. Vasander and J. Laine (1999). Restoration of drained peatlands in southern Finland: initial effects on vegetation change and CO2 balance. *Journal of Applied Ecology* **36**(5): 634-648.

Krug, E. C. and C. R. Frink (1983). Acid-Rain on Acid Soil - a New Perspective. *Science* **221**(4610): 520-525.

Laiho, R., T. Sallantaus and J. Laine (1998): The effect of forestry drainage on the vertical distribution of major plant nutrients in peat soils. *Plant and Soil* **207**: 169-181.

Littlewood, I. G. (1995). Hydrological Regimes, Sampling Strategies, and Assessment of Errors in Mass Load Estimates for United-Kingdom Rivers. *Environment International* **21**(2): 211-220.

Littlewood, I. G., K. Down, J. R. Parker and D. A. Post (1997). IHACRES: Catchment-scale rainfall-streamflow modelling (PC version) Version 1.0 - April 1997., Institute of Hydrology.

LMNO. (1999). "V Notch Weir Discharge Calculator and Equations." Retrieved 18/11/2006, from http://www.lmnoeng.com/Weirs/vweir.htm.

Lumsdon, D. G., M. I. Stutter, R. J. Cooper and J. R. Manson (2005). Model assessment of biogeochemical controls on dissolved organic carbon partitioning in an acid organic soil. *Environmental Science & Technology* **39**(20): 8057-8063.

Manly, B. F. J. (1986). *Multivariate Statistical Methods: A Primer*. London, Chapman & Hall.

Martens, H. and M. Martens (2000). Modified Jack-knife estimation of parameter uncertainty in bilinear modelling by partial least squares regression (PLSR). *Food Quality and Preference* **11**(1-2): 5-16.

Martens, H. and T. Naes (1989). *Multivariate Calibration*. New York, John Wiley and Sons.

McDonald, A. T., G. Mitchell, P. S. Naden and D. S. J. Martin (1991). Discoloured water investigations. Report to Yorkshire Water, University of Leeds.

McKnight, D., E. M. Thurman, R. L. Wershaw and H. Hemond (1985). Biogeochemistry of Aquatic Humic Substances in Thoreau Bog, Concord, Massachusetts. *Ecology* **66**(4): 1339-1352.

Meybeck, M., G. Friedrich, R. Thomas and D. Chapman (1996). Rivers. *Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring - Second Edition*. D. Chapman, UNESCO / WHO / UNEP.

Mitchell, G. and A. T. McDonald (1992). Discoloration of Water by Peat Following Induced Drought and Rainfall Simulation. *Water Research* **26**(3): 321-326.

Mitchell, G. and A. T. McDonald (1995). Catchment Characterization as a Tool for Upland Water-Quality Management. *Journal of Environmental Management* **44**(1): 83-95.

Morris, R. D., A. M. Audet, I. F. Angelillo, T. C. Chalmers and F. Mosteller (1992). Chlorination, Chlorination by-Products, and Cancer - a Metaanalysis. *American Journal of Public Health* **82**(7): 955-963.

Mulder, J., N. Christophersen, K. Kopperud and P. H. Fjeldal (1995). Water-Flow Paths and the Spatial-Distribution of Soils as a Key to Understanding Differences in Streamwater Chemistry between 3 Catchments (Norway). *Water Air and Soil Pollution* **81**(1-2): 67-91.

Naden, P. S. and A. T. McDonald (1989). Statistical Modeling of Water Color in the Uplands - the Upper Nidd Catchment 1979-1987. *Environmental Pollution* **60**(1-2): 141-163.

Neal, C., C. J. Smith, J. Walls and C. S. Dunn (1986). Major, Minor and Trace-Element Mobility in the Acidic Upland Forested Catchment of the Upper River Severn, Mid Wales. *Journal of the Geological Society* **143**: 635-648.

Olive, L. J. and W. A. Rieger (1988). *An examination of the role of sampling strategies in the study of suspended sediment transport.* Sediment Budgets, Porto Alegre, IAHS.

ONS. (2004, 14/09/2004). "Nomenclature of Units for Territorial Statistics (NUTS) / Local Administrative Units (LAUs)." Retrieved 21 November, 2006, from http://www.statistics.gov.uk/geography/nuts.asp.

Osborn, T. J. and M. Hulme (2002). Evidence for trends in heavy rainfall events over the UK. *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **360**(1796): 1313-1325.

Pearsall, W. H. (1956). 2 Blanket-Bogs in Sutherland. *Journal of Ecology* **44**(2): 493-&.

Pearson, K. (1901). On lines and planes of closest fit to a system of points in space. *Philosophical Magazine* **2**: 557-572.

Petersen, W., L. Bertino, U. Callies and E. Zorita (2001). Process identification by principal component analysis of river water-quality data. *Ecological Modelling* **138**(1-3): 193-213.

Phillips, J. and R. Moss (1977). Effects of Subsoil Draining on Heather Moors in Scotland. *Journal of Range Management* **30**(1): 27-29.

Phillips, J. M., B. W. Webb, D. E. Walling and G. J. L. Leeks (1999). Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples. *Hydrological Processes* **13**(7): 1035-1050.

Prevost, M., A. P. Plamondon and P. Belleau (1999). Effects of drainage of a forested peatland on water quality and quantity. *Journal of Hydrology* **214**(1-4): 130-143.

Ratcliffe, D. A. and P. H. Oswald (1988). *The flow country : the peatlands of Caithness and Sutherland*. Nature Conservancy Council, Peterborough.

Robertson, D. M. and E. D. Roerish (1999). Influence of various water quality sampling strategies on load estimates for small streams. *Water Resources Research* **35**(12): 3747-3759.

Rycroft, D. W., D. J. A. Williams and H. A. P. Ingram (1975). The Transmission of Water Through Peat: I. Review. *The Journal of Ecology* **63**(2): 535-556.

Salamander. (2006). "Data Acquisition Systems: Sentry II Datalogger and Sentry Solo." Retrieved 18 November, 2006, from http://www.salamander-group.co.uk/downloads/SentryIIdatalogger.pdf.

Schleppi, P., P. A. Waldner and B. Fritschi (2006). Accuracy and precision of different sampling strategies and flux integration methods for runoff water: comparisons based on measurements of the electrical conductivity. *Hydrological Processes* **20**(2): 395-410.

Scott, M. J., M. N. Jones, C. Woof and E. Tipping (1998). Concentrations and fluxes of dissolved organic carbon in drainage water from an upland peat system. *Environment International* **24**(5-6): 537-546.

Silins, U. and R. L. Rothwell (1998). Forest peatland drainage and subsidence affect soil water retention and transport properties in an Alberta peatland. *Soil Science Society of America Journal* **62**(4): 1048-1056.

Silvola, J., J. Valijoki and H. Aaltonen (1985). Effect of draining and fertilization on soil respiration at three ameliorated peatland soils. *Acta Forestalia Fennica* **191**: 1-32.

Singer, P. C. (1999). Humic substances as precursors for potentially harmful disinfection by-products. *Water Science and Technology* **40**(9): 25-30.

Sjors, H. and U. Gunnarsson (2002). Calcium and pH in north and central Swedish mire waters. *Journal of Ecology* **90**(4): 650-657.

SNH. (2006). "Land Cover Change in Scotland." Retrieved 19 November, 2006, from http://www.snh.org.uk/publications/on-line/education/advances5/4-land-cover.asp.

Sprent, P. (1969). *Models in Regression.* London, Methuen.

Statsoft. (2003). "Partial Least Squares (PLS) / Statsoft Electronic Textbook." Retrieved 20 November, 2006, from http://www.statsoft.com/textbook/stpls.html.

Stephens, N. and L.J. Symons (1956). *The Lough Erne drainage system.* In Suggate, L.S., editor, *This changing world.* Geography **41**, 123–26.

Stevens, J. (1996). *Applied multivariate statistics for the social sciences.* Marwah, New Jersey, Lawrence Erlbaum.

Stewart, A. J. A. and A. N. Lance (1983). Moor-Draining - a Review of Impacts on Land-Use. *Journal of Environmental Management* **17**(1): 81-99.

Stewart, A. J. A. and A. N. Lance (1991). Effects of Moor-Draining on the Hydrology and Vegetation of Northern Pennine Blanket Bog. *Journal of Applied Ecology* **28**(3): 1105-1117.

Sykes, J. M. and A. M. J. Lane (1996). *The United Kingdom Environmental Change Network : protocols for standard measurements at terrestrial sites*. London, The Stationery Office.

Tabachnick, B. G. and L. S. Fidell (1989). *Using Multivariate Statistics*. Cambridge, MA, Harper and Row.

Tarboton, D. G., R. L. Bras and I. Rodrigueziturbe (1991). On the Extraction of Channel Networks from Digital Elevation Data. *Hydrological Processes* **5**(1): 81-100.

Theimer, B. D., D. C. Nobes and B. G. Warner (1994). A Study of the Geoelectrical Properties of Peatlands and Their Influence on Ground-Penetrating Radar Surveying. *Geophysical Prospecting* **42**(3): 179-209.

Thompson, C. K. (1948). HILL DRAINAGE. *Journal of the British Grassland Society* **3**(3): 193-202.

Tipping, E., C. Woof, E. Rigg, A. F. Harrison, P. Ineson, K. Taylor, D. Benham, J. Poskitt, A. P. Rowland, R. Bol and D. D. Harkness (1999). Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. *Environment International* **25**(1): 83-95.

Tranvik, L. J. and M. Jansson (2002). Climate change - Terrestrial export of organic carbon. *Nature* **415**(6874): 861-862.

Tuittila, E. S., V. M. Komulainen, H. Vasander, H. Nykanen, P. J. Martikainen and J. Laine (2000). Methane dynamics of a restored cut-away peatland. *Global Change Biology* **6**(5): 569-581.

Turner, N. (1757). An Essay on Draining and Improving Peat Bogs; in Which Their Nature and Properties Are Fully Considered. London, Baldwin and Pew.

Urban, N. R., S. E. Bayley and S. J. Eisenreich (1989). Export of Dissolved Organic-Carbon and Acidity from Peatlands. *Water Resources Research* **25**(7): 1619-1628.

Vasander, H., E.-S. Tuittila, E. Lode, L. Lundin, M. Ilomets, T. Sallantaus, R. Heikkilä, M.-L. Pitkänen and J. Laine (2003). Status and restoration of peatlands in Northern Europe. *Wetlands Ecology and Management* **11**: 61-63

Vega, M., R. Pardo, E. Barrado and L. Deban (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research* **32**(12): 3581-3592.

Verhoff, F. H. and S. M. Yaksich (1982). Storm Sediment Concentrations as Affected by Land-Use, Hydrology, and Weather. *Journal of Environmental Quality* **11**(1): 72-78.

Vogt, R. D. and I. P. Muniz (1997). Soil and stream water chemistry in a pristine and boggy site in mid-Norway. *Hydrobiologia* **348**: 19-38.

Waddington, J.M. and J. Price, (2000). Effect of peatland drainage, harvesting, and restoration on atmospheric water and carbon exchange. *Physical Geography* **21**: 433-451.

Wallage, Z. E., J. Holden and A. T. McDonald (2006). Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Science of the Total Environment* **367**(2-3): 811-821.

Wallage, Z. E., J. Holden and A. T. McDonald (In review). An unstable dissolved organic carbon concentration and water colour relationship in peatlands. *Water Resources Research.*